

**PRESENCE OF BROMACIL, DIURON, AND SIMAZINE IN SURFACE WATER
RUNOFF FROM AGRICULTURAL FIELDS AND NON-CROP SITES
IN TULARE COUNTY, CALIFORNIA**



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Pest Management Analysis and Planning Program

**STATE OF CALIFORNIA
Department of Food and Agriculture
Division of Pest Management, Environmental Protection and Worker Safety
Environmental Monitoring and Pest Management Branch
1220 N Street, Sacramento, California 95814**

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IN TULARE COUNTY, CALIFORNIA**

By

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FEBRUARY, 1991

PEST MANAGEMENT ANALYSIS & PLANNING PROGRAM

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ABSTRACT

A number of wells in Tulare County have been found to contain residues of the agricultural herbicides bromacil, diuron, and simazine. A better understanding of the possible role of surface runoff water from agricultural fields in transporting pesticides to ground water is needed. Insufficient information is available on the amounts of pesticides present in surface water runoff during winter rain or irrigation. To determine the presence and concentrations of herbicides in runoff water following a rain or irrigation, the Pest Management Analysis and Planning Program (PMAP) of the California Department of Food and Agriculture conducted a survey in Tulare County with the cooperation of the County Agricultural Commissioner, DuPont, and Ciba-Geigy. Such information is crucial in order to design an effective ground water protection strategy.

The herbicides bromacil, diuron, and simazine were detected in surface runoff water from agricultural fields and non-crop sites following a rain or irrigation event. The concentration means and ranges for simazine and diuron in runoff rain water were 367.3 ppb (2.4 ppb to 1,130 ppb) and 219.8 ppb (3.1 ppb to 890.5 ppb), respectively. The mean concentration and range of bromacil detected in runoff rain water was 8.5 ppb (non-detectable to 47.2 ppb). Diuron, simazine, and bromacil concentrations in runoff rain water collected at sites suspected to be dry wells varied from 139.3 ppb to 890.5 ppb, 280.0 ppb to 934.0 ppb, and non-detectable to 8.1 ppb, respectively. Water was running into the suspected dry well at the time of sampling.

When a rain event occurred shortly after pesticide application, surface runoff water usually contained high concentrations of diuron and simazine.

Lower concentrations of bromacil (non-detectable to 4.7 ppb), diuron (non-detectable to 19.1 ppb), and simazine (non-detectable to 25.2 ppb) were detected in runoff water following an irrigation event. Why these concentrations were lower than those detected in runoff rain water is unknown.

To reduce off-field movement of these herbicides, PMAP is currently investigating citrus orchard floor management practices.

ACKNOWLEDGMENTS

We are indebted to Mr. Clyde Churchill, Agricultural Commissioner of Tulare County, and his staff for their cooperation and assistance in this study. We would like to thank Drs. R. A. Jackson and E. W. Zahnow of E. I. DuPont de Nemours & Company, and Drs. R. H. Ross, Jr. and J. Harrison of Ciba-Geigy Corporation for the chemical analyses of the samples and description of the analytical methods.

A very special thanks to Drs. D.J. Weaver, J.J. Troiano, and C.H. Pickett for their critical review of this report.

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INTRODUCTION

A survey by the Environmental Hazards Assessment Program of the California Department of Food and Agriculture (CDFA) of wells in Tulare County, California, revealed that 49% of 122 wells sampled were contaminated with detectable levels of one or more herbicides including simazine (2-chloro-4,6-bis [ethylamino]-s-triazine), diuron (3-[3,4-dichlorophenyl]-1,1-dimethyl-urea), atrazine (2-chloro-4-ethylamino-6-isopropanyl-amino-s-triazine), bromacil (5-bromo-3-sec-butyl-methyluracil), and prometon (2,4-bis[isopropyl-amino]-6-methoxy-s-triazine) (7).

Results from a mailing survey of citrus growers in Tulare County, conducted in 1988 by the Pest Management Analysis and Planning Program (PMAP) of CDFA, indicated that large water applications during winter months may play an important role in ground water contamination by herbicide residues (5). In winter and early spring, water from rainfall, irrigation, and frost protection moves off-site and may carry pesticide residues that could eventually reach ground water. However, little data are available on amounts of pesticides present in water that moves off individual fields in California during the winter (6). A better understanding is needed of the factors that play a role in ground water contamination in order to design an effective prevention strategy.

The objective of this survey was to determine if detectable levels of bromacil, diuron, and simazine are present in surface runoff water from agricultural fields and non-crop sites following a winter rain or irrigation. This objective was achieved through a cooperative effort among PMAP, DuPont de Nemours & Company (DuPont), Ciba-Geigy Corporation, and the Tulare County Agricultural Commissioner (CAC). PMAP coordinated the responsibilities and activities of these groups during the study. The CAC collected and shipped

the samples to the appropriate laboratories. DuPont, Ciba-Geigy, and APPL, Inc. performed the chemical analyses and reported results to PMAP.

MATERIALS AND METHODS

The study area was in the eastern part of Tulare County, California. A total of 29 potential sampling sites were identified by the CAC and the PMAP staff. The following criteria were used for the selection of sampling sites: (1) location within or near a Pesticide Management Zone (PMZ), an area of about one square mile which is known to be sensitive to ground water contamination by one or more pesticides; (2) crop and surrounding crops, namely oranges and grapes; (3) ease in taking samples.

Each site was sampled once, either at the lowest end of the field, in-flow into a drain or suspected dry well, or directly out of a canal or sump. Except at sampling site #2, samples were collected from water running towards the lowest end of the field during or right after a rain or irrigation. Approximately six liters of runoff water were collected in a bucket from a site. The water sample was split into six subsamples by pouring into one liter amber glass bottles which were sealed with Teflon®-lined caps. All bottles were immediately placed on wet ice in an ice chest. Water samples were shipped to Ciba-Geigy in Greensboro, North Carolina, for simazine analyses and to DuPont in Wilmington, Delaware, for diuron and bromacil analyses. All bottles were accompanied by chain of custody records (Appendix I) and packed in Styrofoam® containers, placed in an ice chest and kept cold with wet ice. Ice chests were shipped by Federal Express with overnight arrival at the cooperating laboratories.

Thirty-five percent of the 20 water samples taken were sent for quality control analyses to APPL, Inc. in Fresno, California, a private laboratory.

Analytical procedures were provided by DuPont (Appendix II), Ciba-Geigy (Appendix III), and APPL (Appendix IV). Minimum detection limits for bromacil, diuron, and simazine in water samples were 1.0, 1.0, and 0.1 ppb, respectively.

Ciba-Geigy's and DuPont's analytical results were used for the analyses and interpretation of the data.

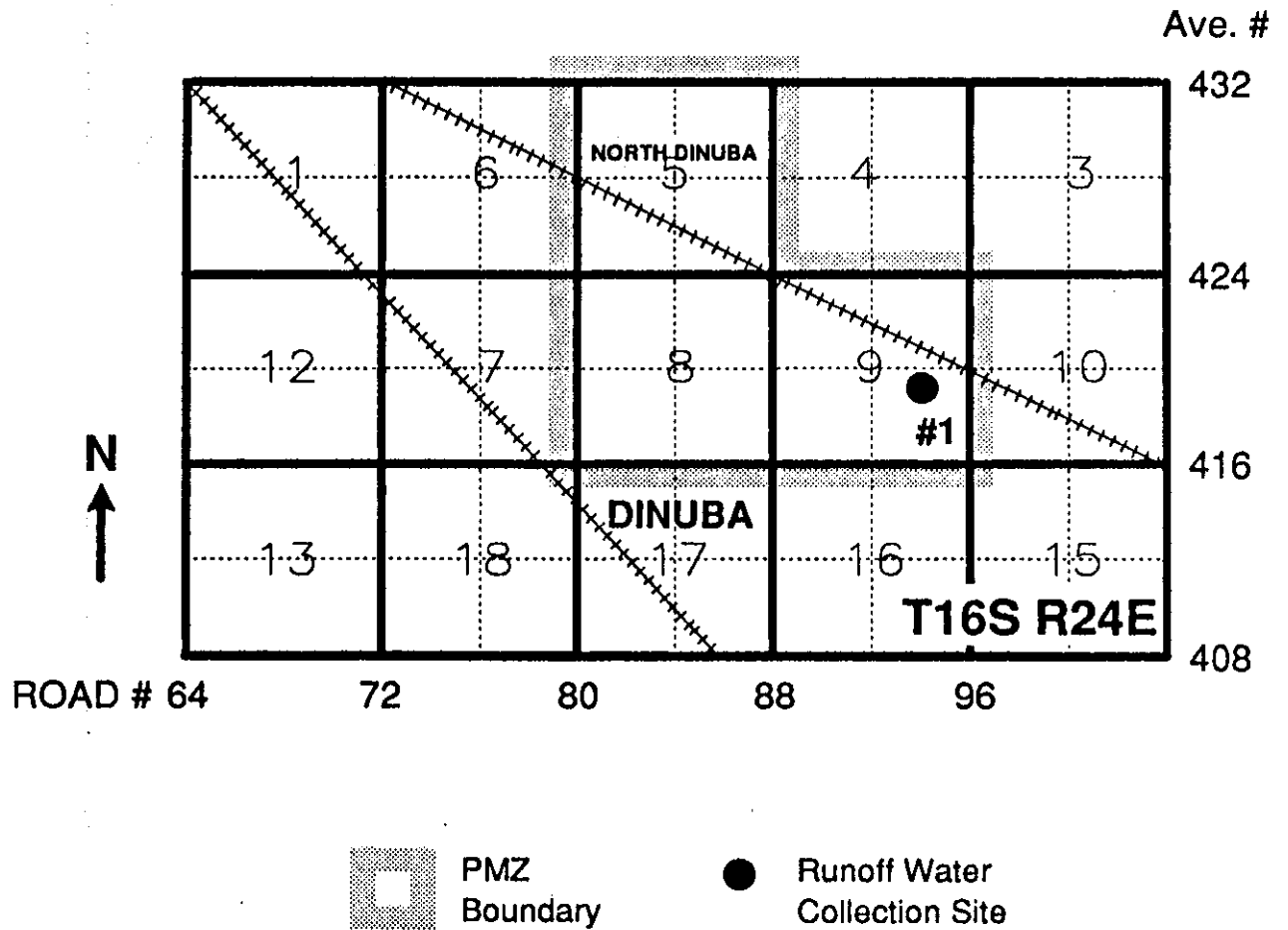
RESULTS AND DISCUSSION

A total of 29 potential sampling sites were identified: 23 post rainfall sites, and 6 post irrigation sites. However, post rainfall samples were taken from only 14 sites because insufficient water was available at the remaining sites when sampling was conducted. All 6 post irrigation sites were sampled.

Location of the sampling sites relative to nearby PMZ locations are presented in Figures 1-9. Site description and information on rates of pesticides applied and pesticide application and sampling dates were provided by the CAC's office (Table 1).

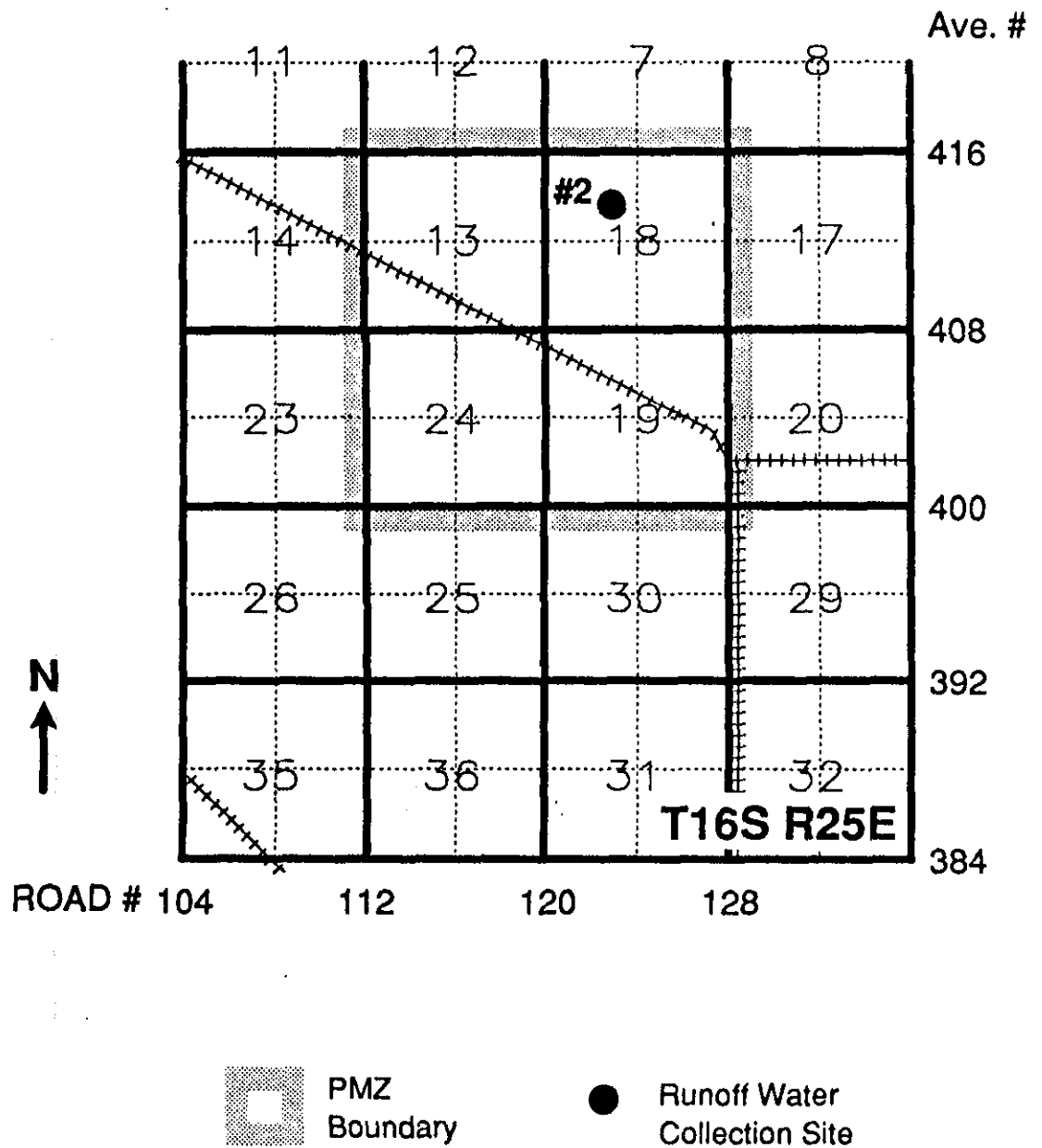
Bromacil, diuron, and simazine were detected in surface runoff water following rain or irrigation events on agricultural fields and non-crop sites (Tables 2 and 3). Simazine and diuron were detected more often than bromacil in runoff water following either rain or irrigation events. The greater frequencies of detection and higher concentrations in runoff water of diuron and simazine compared to bromacil could be attributed to the greater use of simazine and diuron. In 1988, 19,588 lbs. a.i. bromacil, 64,068 lbs. a.i. diuron, and 30,768 lbs. a.i. simazine were used in Tulare County (CAC, personal communication). Pickett et al. (5) showed that simazine and diuron were considered the most important herbicides by citrus growers.

Figure 1. Runoff rain water collection site #1 with reference to Pesticide Management Zones (PMZ) in Tulare County.



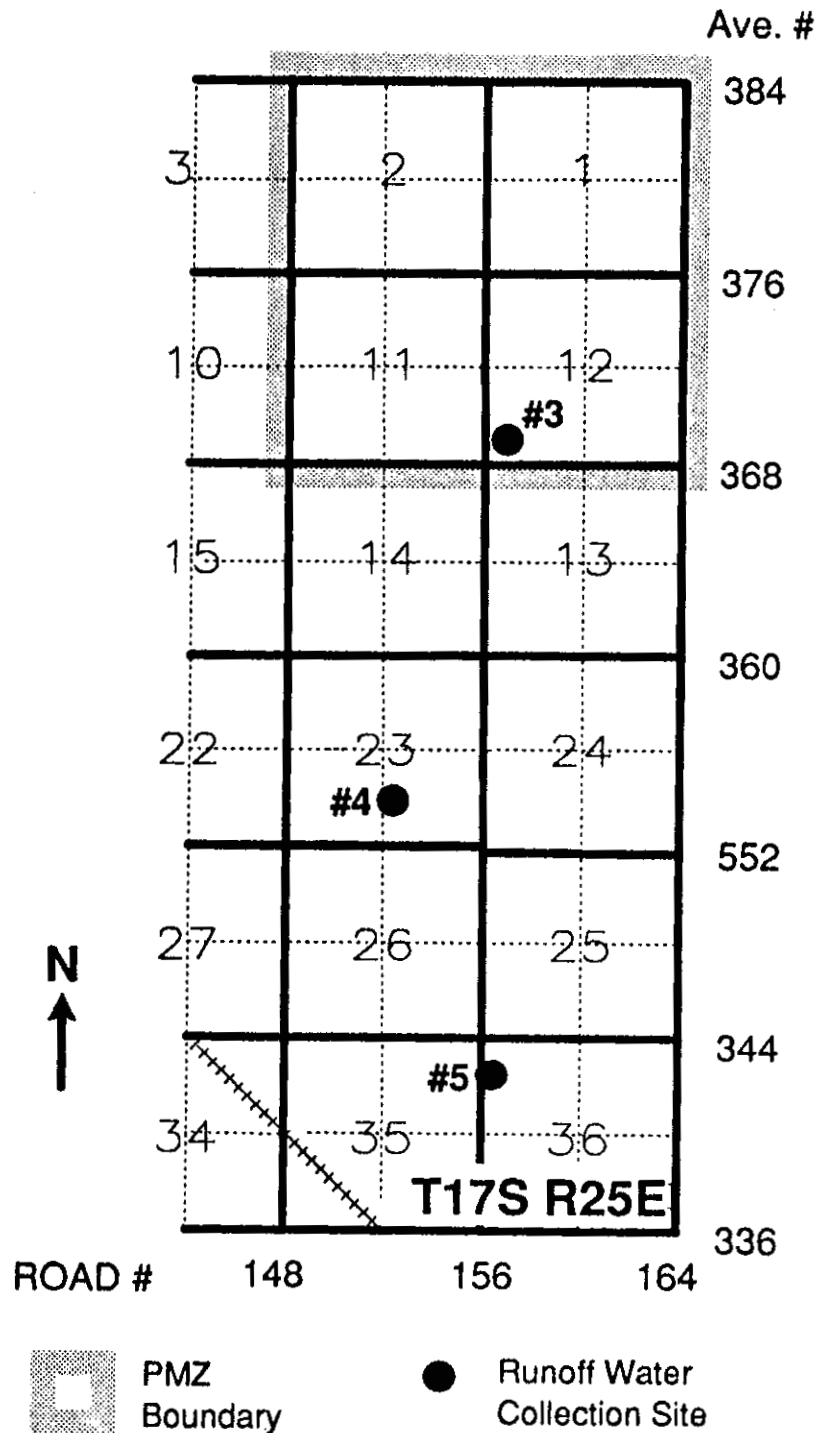
T16SR24E - Township and Range
 Squares with numbers in the center are sections.
 Each section is 1 square mile (1 inch = 1 mile)

Figure 2. Runoff rain water collection site #2 with reference to Pesticide Management Zones (PMZ) in Tulare County.



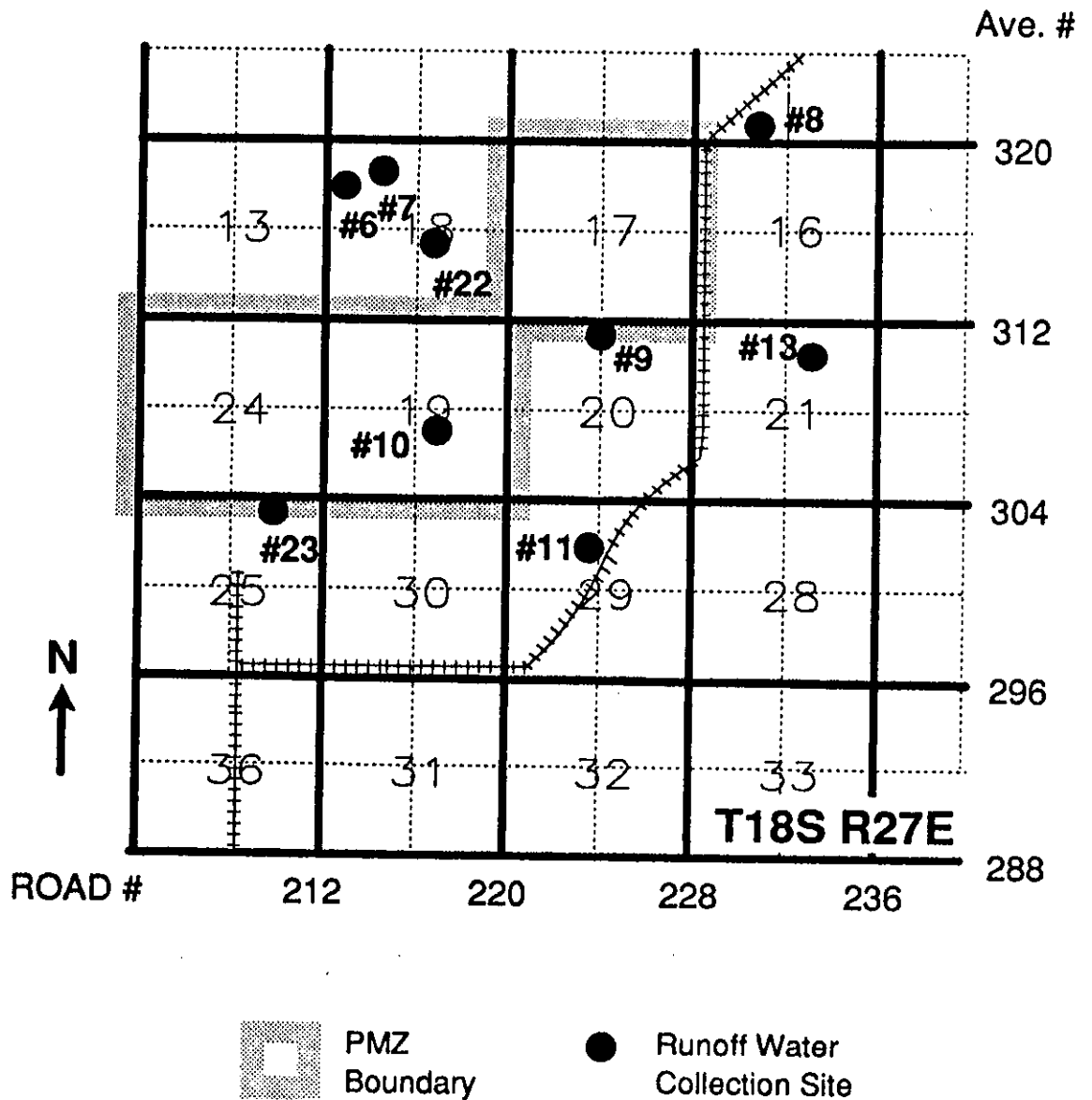
T16SR25E - Township and Range
 Squares with numbers in the center are sections.
 Each section is 1 square mile (1 inch = 1 mile)

Figure 3. Runoff rain water collection sites #3-5 with reference to Pesticide Management Zones (PMZ) in Tulare County.



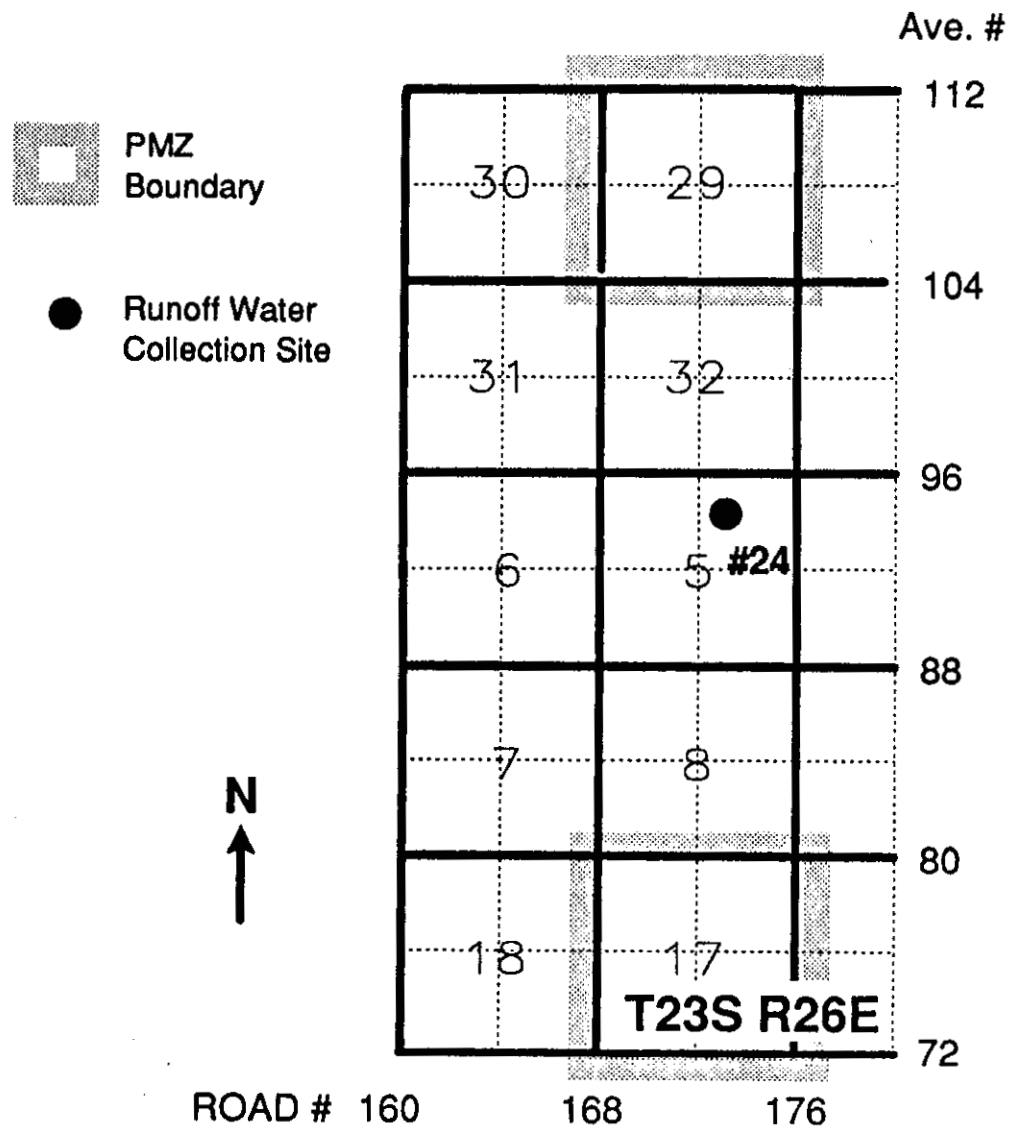
T17SR25E - Township and Range
 Squares with numbers in the center are sections.
 Each section is 1 square mile (1 inch = 1 mile)

Figure 4. Runoff rain water collection sites #6-11, 13, 22, and 23 with reference to Pesticide Management Zones (PMZ) in Tulare County.



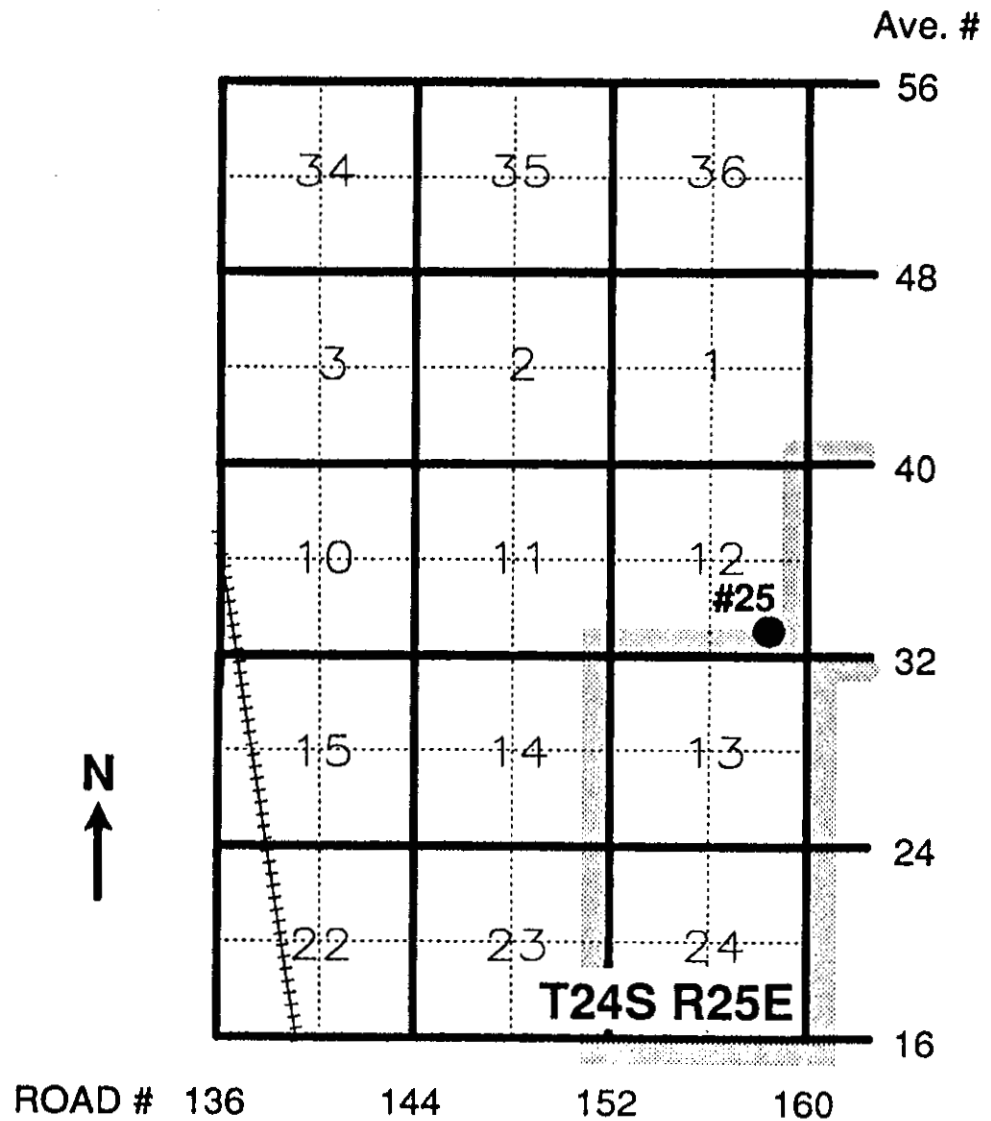
T18SR27E - Township and Range
 Squares with numbers in the center are sections.
 Each section is 1 square mile (1 inch = 1 mile)

Figure 5. Runoff irrigation water collection site #24 with reference to Pesticide Management Zones (PMZ) in Tulare County.



T23SR26E - Township and Range
 Squares with numbers in the center are sections.
 Each section is 1 square mile (1 inch = 1 mile)

Figure 6. Runoff irrigation water collection site #25 with reference to Pesticide Management Zones (PMZ) in Tulare County.



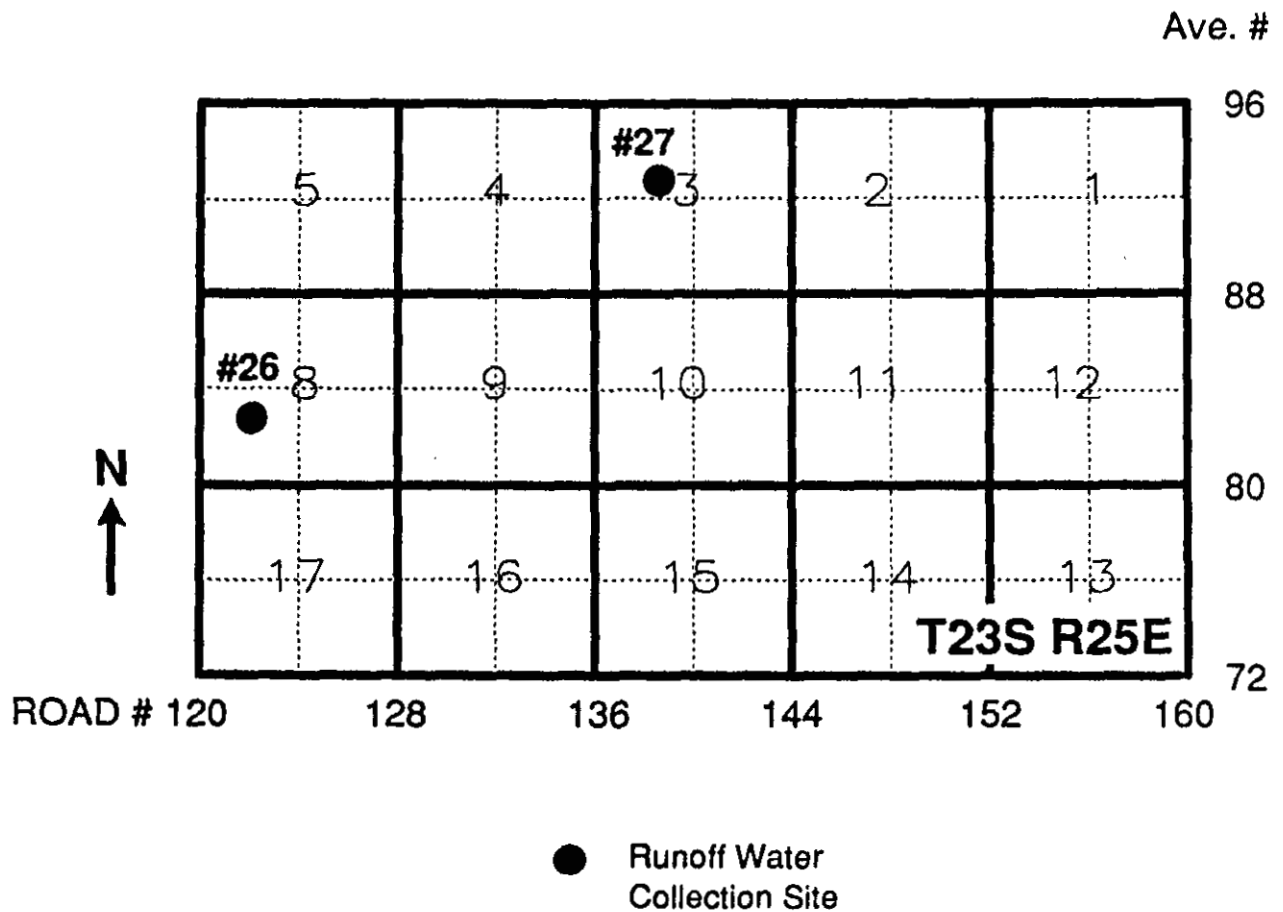
PMZ
Boundary



Runoff Water
Collection Site

T24SR25E - Township and Range
Squares with numbers in the center are sections.
Each section is 1 square mile (1 inch = 1 mile)

Figure 7. Runoff irrigation water collection sites #26 and 27 in Tulare County.

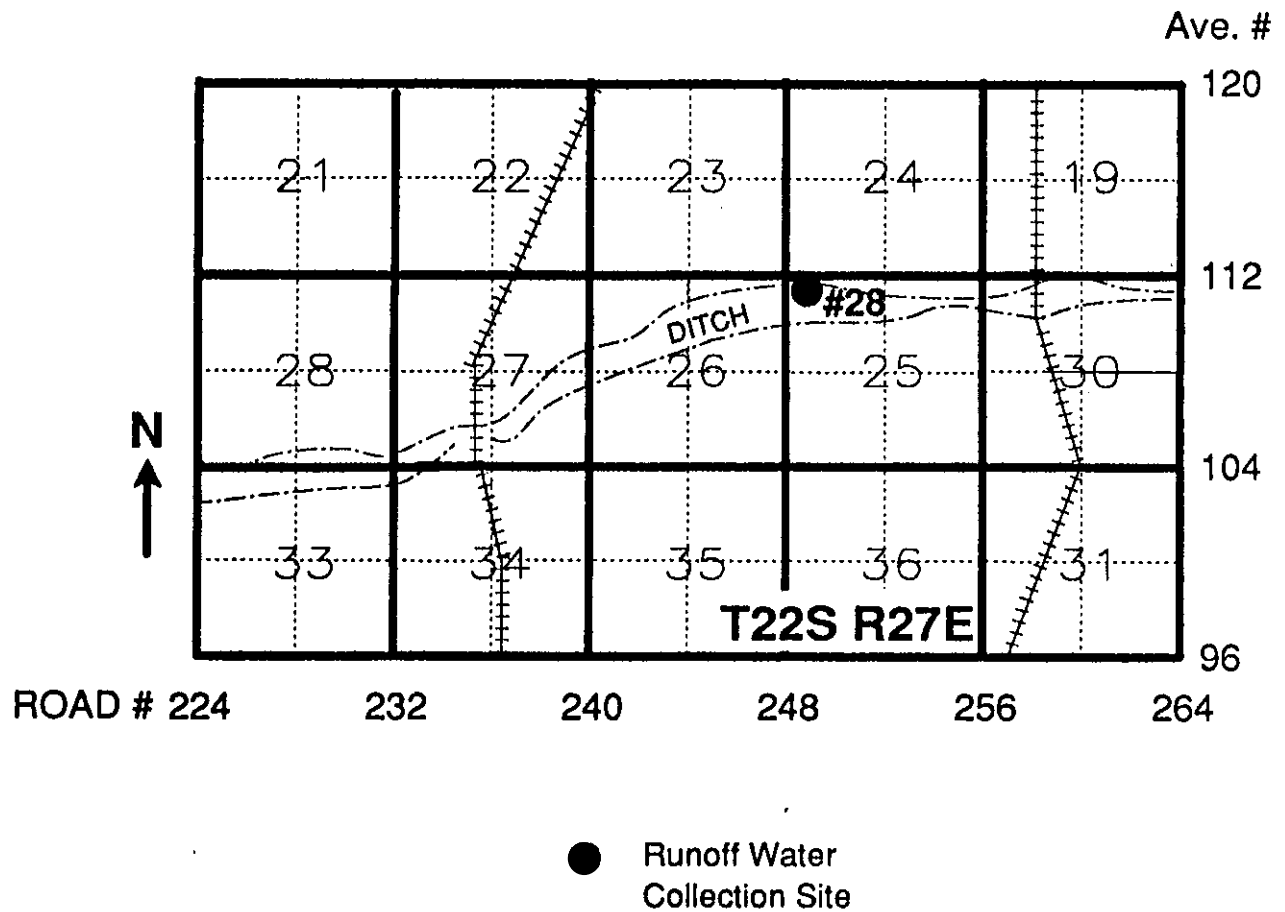


T23SR25E - Township and Range

Squares with numbers in the center are sections.

Each section is 1 square mile (1 inch = 1 mile)

Figure 8. Runoff irrigation water collection site #28 in Tulare County.

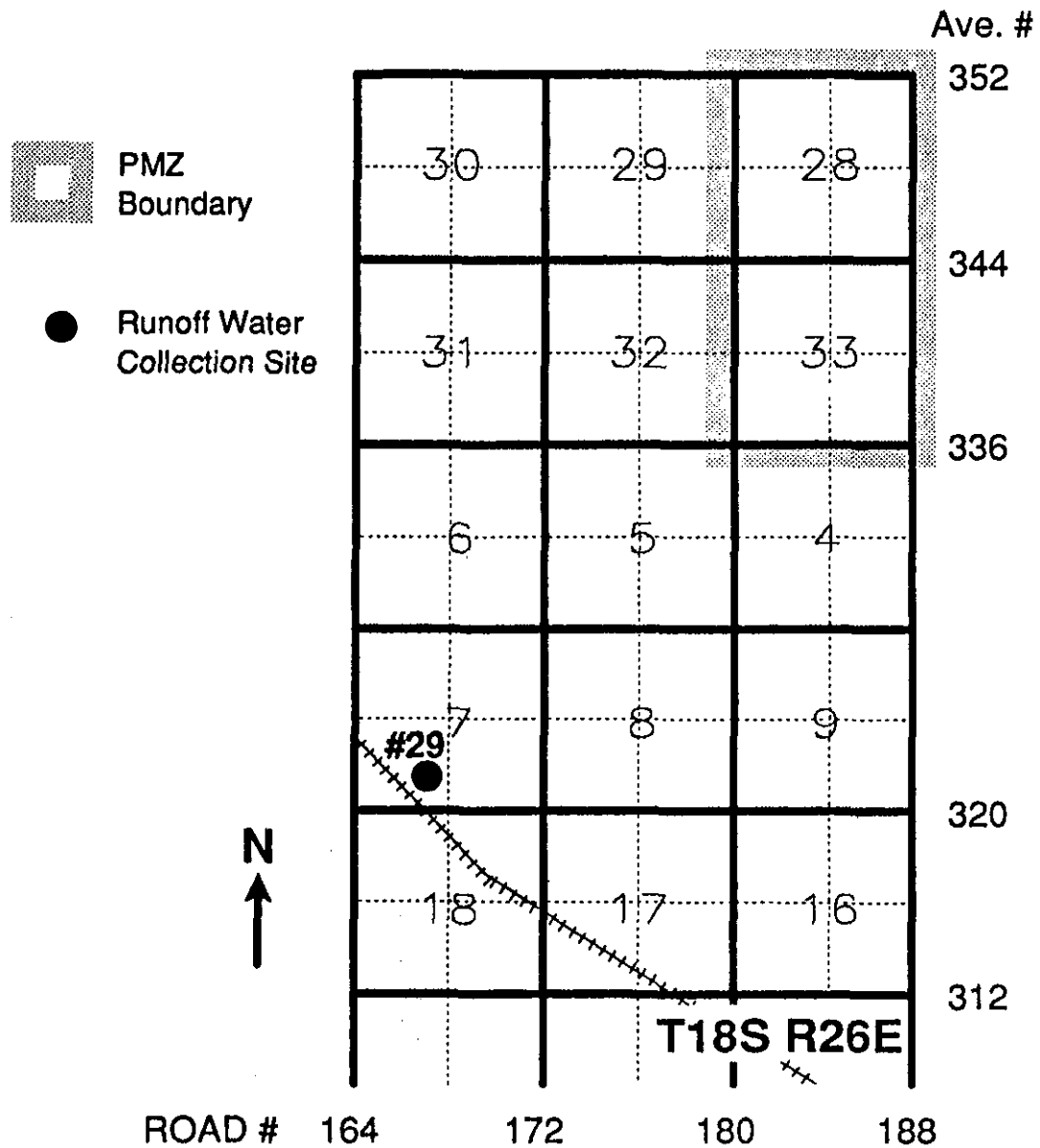


T22SR27E - Township and Range

Squares with numbers in the center are sections.

Each section is 1 square mile (1 inch = 1 mile)

Figure 9. Runoff irrigation water collection site #29 with reference to Pesticide Management Zones (PMZ) in Tulare County.



T18SR26E - Township and Range

Squares with numbers in the center are sections.

Each section is 1 square mile (1 inch = 1 mile)

Table 1. Site Descriptions, Rates, and Dates of Pesticide Applications and Sampling.

Site	Location TRS*	Description	Pesticide Applied & Rate**	Applica- tion Date	Sampling Date	Runoff water due to
1.	16SR24E9	Runoff water originated in orange grove.	Simazine 3 Lbs	11/1/89	1/13/90	Rain
2.	16SR25E18	Same surrounding; mostly open oranges, houses.	Simazine, 2-1/2 Lbs. Diuron, 2 Lbs	2/1/89	1/13/90	Rain
3.	17SR25E12	Secondary site--Runoff water of unknown origin.			1/13/90	Rain
4.	17SR25E23	Runoff water originated in orange grove. Surrounding crops: oranges.	Simazine, 3 Lbs Diuron, 2 Lbs	11/16/89	1/13/90	Rain
5.	17SR25E36	Runoff water originated in orange grove. Surrounding crops: oranges.	Simazine, 1-1/4 Lbs Diuron, 1 Lb	10/30/89	1/13/89	Rain
6.	18SR27E18	Runoff water originated in orange grove. Surrounding crops: oranges, open.	Simazine, 1.2 Lbs Diuron, 1.3 Lbs	11/11/89	1/13/90	Rain
7.	18SR27E18	Runoff water originated in olive orchard. Surrounding crops: olives, oranges, open ground.	Simazine, 4.2 Lbs Diuron, 1.7 Lbs	11/11/89	1/13/90	Rain
8.	18SR27E9	Runoff water originated in orange grove. Surrounding crops: oranges.	Simazine, 5 Lbs Diuron, 3 Lbs	3/1/89	1/13/90	Rain
9.	18SR27E20	Runoff water originated in orange grove. Surrounding crops: oranges.	Simazine, 1.6 Lbs Diuron, 1.3 Lbs	12/13/89	1/14/90	Rain
10.	18SR27E19	Runoff water originated in orange grove. Surrounding crops: oranges.	Simazine, 5 Lbs Diuron, 4 Lbs	3/27/89	1/13/90	Rain
11.	18SR27E29	Runoff water originated in orange grove and along RR tracks. Surrounding crops: oranges.	Simazine, 1.6 Lbs Diuron, 1.3 Lbs	11/1/88	1/16/90	Rain
13.	18SR27E21	Runoff water originated in orange grove. Surrounding crops: citrus, open.	Not available	Not available	1/13/90	Rain
22.	18SR27E19	Runoff water originated in orange grove. Surrounding crops: oranges.	Simazine, 2 Lbs Diuron, 2 Lbs	11/1/88	1/16/90	Rain
23.	18SR26E25	Runoff water originated in orange grove. Surrounding crops: oranges.	Simazine, 2 Lbs Diuron, 2 Lbs	1/19/89	1/16/90	Rain
24.	23SR26E5	Runoff water originated in grapes and the site is surrounded by grapes & wheat.	Not available	2/28/90	3/23/90	Furrow Irrigation

Table 1. Cont'd

Site	Location TRS*	Description	Pesticide Applied & Rate**	Applica- tion Date	Sampling Date	Runoff water due to
25.	24SR25E12	Runoff water originated in grapes which are surrounded by grapes and almonds. No simazine and diuron applied in 1989.	Not available	Not available	3/23/90	Furrow Irrigation
26.	23SR25E8	Runoff water originated in alfalfa hay field. Surrounding crops are grapes, almonds, and fallow ground.	Not available	Not available	3/27/90	Flood Irrigation
27.	23SR25E3	Runoff water originated in grapes which are surrounded by grapes, almonds, and fallow ground.	Not available	Not available	3/27/90	Furrow Irrigation
28.	22SR27E25	Secondary site--Runoff water of unknown origin.			3/28/90	Furrow Irrigation
29.	18SR26E7	Secondary site--Runoff water of unknown origin.			3/28/90	Furrow Irrigation

* TRS = Township, Range, Section.

** Pounds formulated/acre.

In most instances, surface water, following rainfall 1 to 2-1/2 months after pesticide application, contained high concentrations of diuron and simazine (Table 2). This is in agreement with conclusions made by Caro (1) and Wauchope (8) after their literature review on pesticides in agricultural runoff from rainfall.

The concentration mean and range for simazine, diuron, and bromacil in rain water runoff was 367.3 ppb (2.4 ppb to 1,130 ppb), 219.8 ppb (3.1 ppb to 890.5 ppb), and 8.5 ppb (non-detectable to 47.2 ppb), respectively.

Samples of rain runoff collected within orange groves and near suspected dry wells (Figures 10-13), contained high concentrations of diuron and simazine, and significantly lower concentrations of bromacil. Detected concentrations of diuron, simazine, and bromacil ranged from 139.3 ppb to 890.5 ppb, 280.0 ppb to 934.0 ppb, and non-detectable to 8.1 ppb, respectively. At the time of sampling, it was observed that water was running into suspected dry wells. It has been suggested that dry wells may be a direct route for surface water runoff carrying pesticides to move into ground water (2,3,4). There are about 5,000 abandoned dry wells in the Central Valley (4). However, the extent that pesticide-laden runoff water contributes to ground water contamination is still unknown and should be further investigated.

Lower concentrations of herbicides were found in runoff water following irrigation events (Table 3). The mean concentration and range for simazine, diuron, and bromacil in irrigation water runoff was 5.3 ppb (non-detectable to 25.2 ppb), 4.0 ppb (non-detectable to 19.1 ppb), and 0.8 ppb (non-detectable to 4.7 ppb), respectively. Why these pesticide concentrations were lower than in runoff rain water could not be explained by this study.

Table 2. Concentrations (ppb*) of bromacil, diuron, and simazine in runoff water samples collected during a rainfall at different locations in Tulare County.

Sampling Site #	Interval (month) between application and sampling date	Bromacil		Diuron		Simazine	
		DuPont**	APPL***	DuPont**	APPL***	Ciba-Geigy	APPL***
1	2-1/2	47.2±0.3		6.1±0.0		1130.0	
2	10-1/2	4.1±0.2		3.2±0.1		6.8	
3	Unknown	46.6±1.3	101.4±20.6	314.8±17.5	336.7±101.2	215.0	93.8±37.8
4	2	8.1±0.1		890.5±9.7		934.0	
5	2-1/2	ND ^a		139.3±11.1		280.0	
6	2	ND		100.4±12.6		450.0	
7	2	ND		158.8±10.1		535.0	
8	10-1/2	2.3±1.7		78.7±5.1		80.0	
9	1	3.5±1.2		417.5±22.0		465.0	
10	9-1/2	1.4±1.1		449.0±11.5		368.0	
11	14-1/2	ND		38.3±0.8		2.4	
13	Unknown	1.2±0.2		238.8±15.5		331.0	
22	14-1/2	4.0±0.3		240.0±3.8		342.0	
23	12	ND		3.1±0.7		3.0	

^aND - Not detectable. Minimum detection limits for bromacil, diuron, and simazine were 1.0, 1.0, and 0.1 ppb, respectively.

* ppb - parts per billion.

** Average of 4 analyses and their standard deviations.

*** Average of 3 analyses and their standard deviations.

Discrepancies in results (site 3: bromacil and simazine) between APPL and DuPont/Ciba-Geigy may be due to different analytical methods used, and preparation and clean-up of the samples before analysis.



Figure 10. Sampling site #4 at a suspected dry well (arrow) in an orange grove in Tulare County. A runoff rain water sample collected at this site contained 8.1 ppb bromacil, 890.5 ppb diuron, and 934.0 ppb simazine. Water was running into the suspected dry well at the time of sampling.



Figure 11. Sampling site #5 at a suspected dry well (arrow) in an orange grove in Tulare County. A runoff rain water sample collected at this site contained 139.3 ppb diuron and 280.0 ppb simazine. Bromacil was non-detectable. Water was running into the suspected dry well at the time of sampling.



Figure 12. Sampling site #13 at a suspected dry well (arrow) in Tulare County. An orange grove is in the background. A runoff rain water sample at this site contained 1.2 ppb bromacil, 238 ppb diuron, and 331.0 ppb simazine. Water was running into the suspected dry well at the time of sampling.

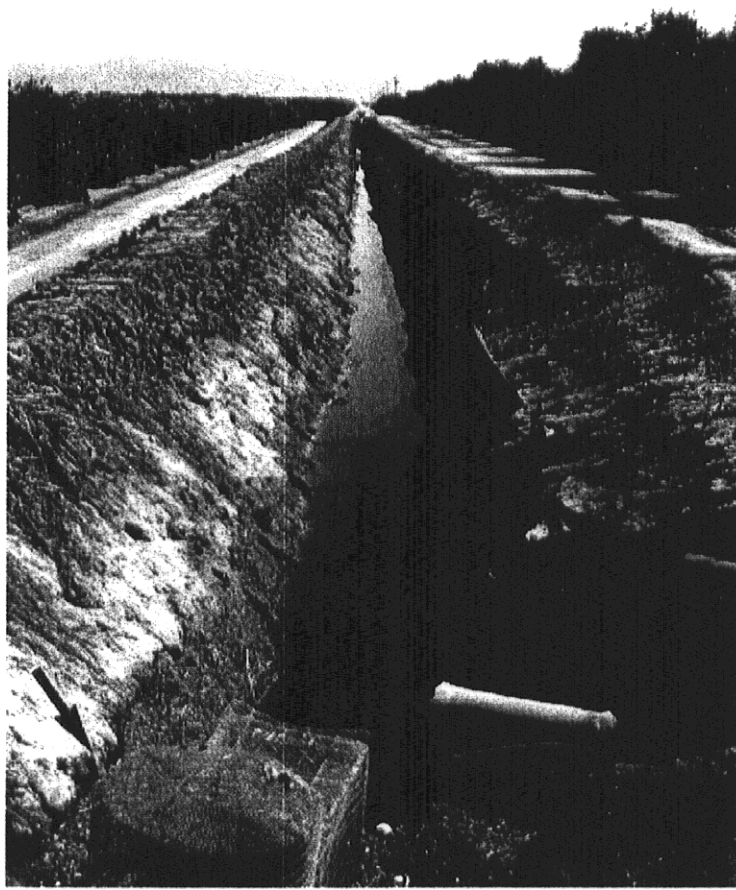


Figure 13. Sampling site #22 at a suspected dry well (arrow) in Tulare County. A runoff rain water sample collected at this site contained 4.0 ppb bromacil, 240.0 ppb diuron, and 342.0 ppb simazine. Water was running into the suspected dry well at the time of sampling.

Table 3. Concentrations (ppb*) of bromacil, diuron, and simazine in runoff water samples collected during irrigation at different locations in Tulare County.

Sampling Site #	Bromacil		Diuron		Simazine	
	DuPont**	APPL***	DuPont**	APPL***	Ciba-Geigy	APPL***
24	ND ^a	ND	2.5±0.1	1.8±0.2	4.3	1.7±0.1
25	ND	ND	ND	0.3±0.1	0.3	0.2±0.0
26	4.7±0.3	ND	ND	1.7±0.4	ND	0.3±0.1
27	ND	ND	19.1±0.3	16.5±1.8	25.2	7.6±0.8
28	ND	ND	ND	ND	0.1	0.1±0.0
29	ND	0.6±0.2	2.1±0.2	1.9±0.2	1.7	2.4±0.3

^aND - Not detectable. Minimum detection limits for bromacil, diuron, and simazine were 1.0, 1.0, and 0.1 ppb, respectively.

* ppb - parts per billion

** Average of 4 analyses and their standard deviations.

*** Average of 3 analyses and their standard deviations.

Discrepancies in results (sites 26 and 27 for simazine) between APPL and DuPont/Ciba-Geigy may be due to different analytical methods used, and preparation and clean-up of the samples before analysis.

Based on the findings of this survey and those of Pickett et al. (5), PMAP is currently investigating citrus orchards floor management practices to reduce off-field movement of these herbicides.

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A P P E N D I X I

CHAIN OF CUSTODY RECORD

ENVIRON. MONITOR. & PEST MGMT.
ENVIRON. HAZARDS ASSESSMENT
1220 N STREET, ROOM A-149
SACRAMENTO, CA 95814

Partner:	Field Location:	<u>Lab Results:</u>		Save Extracts mdl
<u>Remarks:</u> Pesticide(s) Applied: Application Method: Rate/Acre: Pesticide Formulation:		Simazine		
		Bromacil		
		Diuron		
		Chemist:	Analysis Date : Extracted Date:	
		Relinquished for Lab by: (sign)	Date/Time	
<u>KEY</u> <u>Col 1</u> S = Split <u>Col. 77-8 Lab Code</u> 4500 = Ciba-Geigy 4510 = DuPont 2371 = Appl		Received by: (sign)	Relinquished by: (sign)	Date/Time
		Received by: (sign)	Relinquished by: (sign)	Date/Time
		Received by: (sign)	Relinquished by: (sign)	Date/Time
		Received by: (sign)	Relinquished by: (sign)	Date/Time
		Received by: (sign)	Relinquished by: (sign)	Date/Time
		Received for Lab by: (sign)	Date/Time	Lab #

I-1

A P P E N D I X I I

DuPONT'S PESTICIDE ANALYTICAL METHOD



E. I. DU PONT DE NEMOURS & COMPANY
INCORPORATED

WALKER'S MILL, BARLEY MILL PLAZA
P.O. Box 80038
WILMINGTON, DELAWARE 19880-0038

March 19, 1990

AGRICULTURAL PRODUCTS DEPARTMENT

Adolf L. Braun
Pest Management Analysis and Planning Program
Environmental Monitoring and Pest Management
Department of Food & Agriculture
1220 N Street, Room A-149
Sacramento, CA 95814

Dear Mr. Braun

Attached is a report of the analytical results for bromacil and diuron in the runoff water samples from Tulare County that you sent to us. Also included are the Chain of Custody records for these samples.

The presence and concentration of bromacil and diuron was confirmed in selected samples by HPLC/Mass Spectrometry using selected ion monitoring. Bromacil was monitored at m/e 263 and diuron at m/e 233.

<u>Sample</u>	<u>Bromacil (ppb)</u>	<u>Diuron (ppb)</u>
Site 1 Dup 7	43	3
Site 1 Dup 8	44	3
Site 2 Dup 9	4	2
Site 2 Dup 10	3	2
Site 3 Dup 5	45	345
Site 3 Dup 6	43	337
Site 4 Dup 15	4	834
Site 4 Dup 15 (dup)	4	869
Site 4 Dup 16	5	897

We are pleased to have the opportunity to cooperate with CDFA in these studies. We believe that they will help determine the role that surface runoff water plays in transporting chemicals to groundwater via poorly constructed wells or dry wells which were installed to carry runoff water directly to the water table, etc..

Please call me at (302) 992-6268 if you have any questions.

Sincerely,

R A Jackson

R. A. Jackson, Ph.D.
Manager, Ground Water Programs

E. I. DU PONT DE NEMOURS & CO.
AGRICULTURAL PRODUCTS DEPARTMENT
EXPERIMENTAL STATION
WILMINGTON, DELAWARE 19880-0402

cc: J. B. Carr
J. E. Conaway
M. H. Russell, BMP

February 15, 1990

R. A. Jackson
Agricultural Products Department
Barley Mill Plaza, Walker's Mill Bldg.

ANALYSIS OF WATER FOR BROMACIL AND DIURON

The state of California has initiated a study of the role which surface runoff water plays in the contamination of groundwater, and three herbicides (bromacil, diuron and simazine) are being monitored at this time.

Samples are being collected in Tulare County, California by personnel from the County Agricultural Commissioner's Office, and these are then sent to the appropriate laboratories for analysis. Du Pont has assumed responsibility for the analysis of bromacil and diuron.

A copy of the protocol is shown in Appendix I.

As received, all of the samples showed some sediment present. Therefore, about half of each original sample (excepting field fortifications) was filtered through a 20 μ m polyethylene filter (Analytichem Part No. 607520). Portions for analysis were taken from these filtrates.

The results obtained for bromacil and diuron are shown in Tables 1 and 2. Confirmation of the presence of bromacil and diuron has been obtained in selected samples by spectral matching using a photodiode array detector. Additional confirmatory work using mass spectrometry is in progress. Values for the recovery corrections were obtained from Tables 7 and 8.

This study was conducted according to applicable good laboratory practice and meets all requirements to the best of our knowledge.

Edward W. Zahnow
Edward W. Zahnow
Research Associate
(302) 695-1433

February 19, 1990
Date

Robert M. Henze
Robert M. Henze
Laboratory Technician
(302) 695-4007

February 19, 1990
Date

Paul A. Montz
Paul A. Montz
Laboratory Technician
(302) 695-4007

February 19, 1990
Date

APPENDIX II

SAMPLING AND MEASUREMENT

Procedure

The procedure is described in AMR-553-86, Revision 3. Chromatographic information collection and calculations of extract concentrations were performed by the VAX Multichrom System.

Standards

The bromacil standard (N976-120, 8205-69) had a purity of 99.8%, whereas the diuron standard (14740-13, 8205-153) had a purity of 100.0%. These were obtained from the Agricultural Products Department of the Du Pont Company.

Fortification

The samples were fortified (laboratory and matrix), after having been weighed into glass beakers, by pipetting suitable volumes of standard solutions into them and mixing them thoroughly. The samples were then processed as described in the procedure.

Field fortification samples were prepared by pipetting known volumes of standard solutions of bromacil and diuron into 500-mL sample bottles (I-Chem 349-0500) in the laboratory, followed by evaporation of the solvent (methylene chloride). These bottles were then shipped to the field test sites where 450 mL of distilled water were measured into each bottle. The bottles were shipped to the laboratory with the other samples which had been collected.

Sample Data

Shipped: 1/22/90

Received: 1/23/90

Sampled: 1/13, 16, 17/90

Investigators: California Dept. of Food and Agriculture

Notebook Reference: AG0314, pp. 31-75

TABLE 7**Bromacil Recovery**

<u>Fortification Type</u>	<u>Fortification Level (ppb)</u>	<u>Recovery (%)</u>
Laboratory		
(Milli-Q Water)	1.0	86, 90
	2.0	98, 88
	4.0	94, 74
	10.0	117, 92
	20.0	90, 95
	40.0	93, 85
	100	82
Field		
(Distilled Water)	1.1	91, 91
	11.1	94, 92
	111	89, 87
Matrix		
Site 1 Dup 7	200	96
" 2 " 9	20.0	98
" " " 10	4.0	94
" 11 " 30	100	95
" 23 " 1	10.0	99

TABLE 8
Diuron Recovery

<u>Fortification Type</u>	<u>Fortification Level (ppb)</u>	<u>Recovery (%)</u>
Laboratory		
(Milli-Q Water)	1.0	89, 96, 94, 100, 86
	2.0	96, 88
	4.0	86, 84
	10.0	116, 85, 81
	20.0	93, 96, 91
	100	101
Field		
(Distilled Water)	1.1	89, 89
	11.1	99, 96
	111	99, 96
Matrix		
Site 1 Dup 7	200	105
" 2 " 9	20.0	104
" " " 10	4.0	94
" 11 " 30	100	98
" 23 " 1	10.0	111



AGRICULTURAL PRODUCTS
Walker's Mill, Barley Mill Plaza
P.O. Box 80038
Wilmington, Delaware 19880-0038

May 2, 1990

Adolf L. Braun
Pest Management Analysis and Planning Program
Environmental Monitoring and Pest Management
Department of Food & Agriculture
1220 N Street, Room A-149
Sacramento, CA 95814

Dear Mr. Braun:

Attached is a report of the analytical results for bromacil and diuron in the second set of runoff water samples from Tulare County that you sent to us. Also included are the Chain of Custody records for these samples.

We are pleased to continue to cooperate with CDFA in these studies. We believe that they will help determine the role that surface runoff water plays in transporting chemicals to groundwater via poorly constructed wells or dry wells which were installed to carry runoff water directly to the water table, etc..

Please call me at (302) 992-6268 if you have any questions.

Sincerely,

A handwritten signature in cursive script that reads "R. A. Jackson".

R. A. Jackson, Ph.D.
Manager, Ground Water Programs

E. I. DU PONT DE NEMOURS AND COMPANY
AGRICULTURAL PRODUCTS DEPARTMENT
EXPERIMENTAL STATION
WILMINGTON, DELAWARE 19880-0402

cc: J. B. Carr
J. E. Conaway
M. H. Russell, BMP

April 19, 1990

R. A. Jackson
Agricultural Products Department
Barley Mill Plaza, Walker's Mill Bldg.

AMR-1752-90
ANALYSIS OF WATER FOR BROMACIL AND DIURON

This report documents the results of a continuation of the runoff study in Tulare County, California. The study protocol and the results from the initial round of sampling are contained in my report to you dated February 15, 1990.

As received, all of the samples showed some sediment present. Therefore, about half of each original sample (except field fortifications) was filtered through a 20 μ m polyethylene filter (Analytichem Part No. 607520). Portions for analysis were taken from these filtrates.

The results obtained for bromacil and diuron are shown in Tables 1 and 2. Recovery information is given in Tables 3 and 4.

E. W. Zahnow

E. W. Zahnow

EWZ/drb

This study was conducted according to applicable good laboratory practice and meets all requirements to the best of our knowledge.

Edward W. Zahnow
Edward W. Zahnow
Research Associate
(302) 695-1433

April 20, 1990
Date

Robert M. Henze
Robert M. Henze
Laboratory Technician
(302) 695-4007

April 20, 1990
Date

Paul A. Montz
Paul A. Montz
Laboratory Technician
(302) 695-4007

April 20, 1990
Date

APPENDIX I

SAMPLING AND MEASUREMENT

Procedure

The procedure is described in AMR-553-86, Revision 3. Chromatographic information collection and calculations of extract concentrations were performed by the VAX Multichrom System.

Standards

The bromacil standard (N976-120, 8205-69) had a purity of 99.8%, whereas the diuron standard (14740-13, 8205-153) had a purity of 100.0%. These were obtained from the Agricultural Products Department of the Du Pont Company.

Fortification

The samples were fortified (laboratory and matrix), after having been weighed into glass beakers, by pipetting suitable volumes of standard solutions into them and mixing them thoroughly. The samples were then processed as described in the procedure.

Field fortification samples were prepared by pipetting known volumes of standard solutions of bromacil and diuron into 500-mL sample bottles (I-Chem 349-0500) in the laboratory, followed by evaporation of the solvent (methylene chloride). These bottles were then shipped to the field test sites where 450 mL of distilled water were measured into each bottle. The bottles were shipped to the laboratory with the other samples which had been collected.

Sample Data

Shipped:	4/2/90
Received:	4/3/90
Sampled:	3/23, 27-29/90
Investigators:	California Dept. of Food and Agriculture
Notebook Reference:	AG0314, pp. 92-106

TABLE 3**Bromacil Recovery**

<u>Fortification Type</u>	<u>Fortification Level (ppb)</u>	<u>Recovery (%)</u>
Laboratory		
(Milli-Q Water)	1.0	84
	2.0	84
	4.0	90
	10.0	88
	20.0	93
	40.0	90
Field		
(Distilled Water)	1.1	100
	11.1	84
	111	82
Matrix		
Site 24 Sample 36	10.0	89
" 25 " 37	2.0	104
" 26 " 33	20.0	70
" 27 " 39	60.0	90
" 28 " 34	4.0	88
" 29 " 23	10.0	92

TABLE 4**Diuron Recovery**

<u>Fortification Type</u>	<u>Fortification Level (ppb)</u>	<u>Recovery (%)</u>
Laboratory		
(Milli-Q Water)	1.0	82, 94
	2.0	87
	4.0	91
	10.0	91
	20.0	95
Field		
(Distilled Water)	1.1	90
	11.1	92
	111	93
Matrix		
Site 24 Sample 36	10.0	94
" 25 " 37	2.0	107
" 26 " 33	20.0	95
" 27 " 39	60.0	98
" 28 " 34	4.0	95
" 29 " 23	10.0	96



AGRICULTURAL PRODUCTS
Experimental Station
P.O. Box 80402
Wilmington, Delaware 19880-0402

October 3, 1990

Dr. Adolph Braun
California Department of Food and Agriculture
1220 N Street
P. O. Box 942871
Sacramento, CA 94271-0001

Dear Adolph:

In response to your letter of September 26, 1990, I am enclosing a copy of AMR-553-86, Revision 3, August 10, 1988, "Analysis of the Herbicide Bromacil and Diuron in Water".

I understand that this information will be included in the report of the cooperative monitoring study of herbicides in surface runoff water in Tulare County, and I look forward to receiving a copy of this report.

Let me know if I can be of further help.

Best Wishes,

A handwritten signature in cursive script, appearing to read "Ed", positioned above the typed name.

Edward W. Zahnow
Research Associate

/cw
enc.

TRADE SECRET

Study Title

ANALYSIS OF THE HERBICIDES BROMACIL® AND DIURON® IN WATER

Data Requirement

U.S. EPA Pesticide Assessment Guidelines
Subdivision 0, 171-4

Author

E. W. Zahnow
Research Associate

Study Completed On

December 12, 1986

Performing Laboratory

E. I. du Pont de Nemours & Company, Inc.
Agricultural Products Department
Research and Development Division
Experimental Station
Wilmington, Delaware 19898

Laboratory Project ID

AMR-553-86

STATEMENT OF NO DATA CONFIDENTIALITY CLAIMS

No claim of confidentiality is made for any information contained in this study on the basis of its falling within the scope of FIFRA Section 10(d) (1)(A), (B), or (C).

Company E. I. du Pont de Nemours and Company, Inc.

Company Agent _____ Date _____
(Typed Name)

Registration Specialist _____
(Title) (Signature)

We have submitted this material to the United States Environmental Protection Agency specifically under the provisions contained in FIFRA as amended, and thereby consent to use and disclosure of this material by EPA according to FIFRA. Notwithstanding the wording of our marking "TRADE SECRET", this marking by itself conveys no supplemental claims of confidentiality under FIFRA Sections 10(a) or 10(b). In submitting this material to the EPA according to method and format requirements contained in PR Notice 86-5, we do not waive any protection or right involving this material that would have been claimed by the company if this material had not been submitted to the EPA, nor do we waive any protection or right provided under FIFRA Section 10(g).

GOOD LABORATORY PRACTICE STATEMENT

The GLP requirements specified in 40 CFR Part 160 are not applicable to residue data chemistry requirements at the time of submission.

This study was conducted in the spirit of good laboratory practices.

Study Director E. W. Zahnow Date December 18, 1986

Submitter E. I. du Pont de Nemours and Company, Inc.

Sponsor E. I. du Pont de Nemours and Company, Inc.

E. W. Zahnow, Research Associate E. W. Zahnow

R. M. Henze, Lab Technician Trainee R. M. Henze

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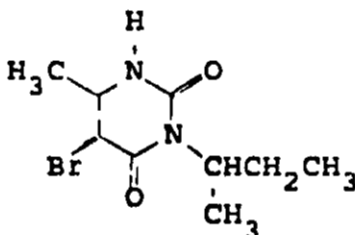
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INTRODUCTION

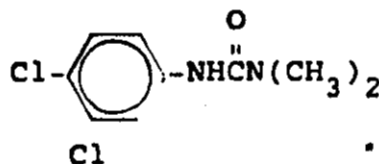
An analytical method based on the use of a liquid chromatograph and a fixed-wavelength, UV absorbance detector is described for the simultaneous determination of bromacil and diuron in water. A straightforward isolation step makes it possible to measure these two compounds at a level of 1 ppb.

Recoveries of 85% or greater have been obtained with bromacil from the detection limit (1 ppb) to a fortification level 20 times greater (20 ppb), whereas with diuron the recoveries were 92% or greater over the same concentration range with individually-fortified samples. Simultaneously-fortified samples result in somewhat lower diuron recoveries.

The structures of the compounds are shown below.



Bromacil



Diuron

EXPERIMENTAL SECTION

Apparatus and Reagents

Liquid Chromatograph - Du Pont Model 8800 equipped with controller, pump and column oven (Du Pont Instruments).

Detector - Du Pont Model 850 Absorbance Detector (Du Pont Instruments).

Injection System - Waters WISP 710B Auto-Sampler (Waters Chromatography Division, Millipore Corporation).

Chromatographic Column - Zorbax® ODS, 4.6 mm i.d. x 25 cm (Du Pont Instruments).

Recorder - HP Model 7130A, 1 millivolt (Hewlett-Packard Corporation).

Nitrogen Evaporator - N-Evap® (Organomation Associates).

Sample Mixer - Vortex-Genie® test tube mixer (Fisher Scientific).

Filtration Equipment - Type XX10 04720 and Type XX15 04700 apparatus; Type HVLP 04700 filters; Millex®-HV filter units (Millipore Corporation).

Storage Bottles - amber, glass with Teflon-lined closures, #349-0500 (I-Chem Research, 23787-F Eichler Street, Hayward, California).

Acetonitrile - HPLC grade (Fisher Scientific).

C₁₈ Sep-Pak® Cartridges - Part 51910 (Waters Chromatography Division, Millipore Corporation).

Bromacil - analytical standard grade (Agricultural Products Department, Research Division, Du Pont Company).

Diuron - analytical standard grade (Agricultural Products Department, Research Division, Du Pont Company).

Preliminary Treatment

Samples should be taken directly into amber glass bottles (suitably cleaned) fitted with Teflon-lined caps. Precleaned bottles, liners and caps are available from I-Chem Research.

If bottles, liners and caps from other sources are used, they should be cleaned as follows:

- (1) Wash in hot tap water with laboratory grade non-phosphate detergent.
- (2) Rinse three times with tap water.
- (3) Rinse with 1:1 nitric acid.
- (4) Rinse three times with ASTM-Type I deionized water.
- (5) Rinse with pesticide grade methylene chloride.
- (6) Rinse once with water as in (4).
- (7) Oven dry at 110°C.
- (8) After the bottles, liners and caps have been removed from the oven and cooled, place liners in caps and caps on bottles as soon as possible. Anyone assembling the containers should wear gloves.

Once taken, the samples should be kept in crushed ice until they can be refrigerated at 4°C.

Processing Procedure

Wash a C₁₈ Sep-Pak[®] with 5 mL of acetonitrile followed by 5 mL of Milli-Q[®] water (obtained from Milli-Q[®] water system,

Millipore Corp.). The flow rate should be such that discrete drops can be seen forming.

Measure a 50-g sample of water, and pass this through the Sep-Pak®. Rinse the sample container with 5 mL of Milli-Q® water, and pass this through the Sep-Pak® also. Discard all liquids up to this point.

Put 5 mL of acetonitrile through the Sep-Pak®, and collect the liquid in a small centrifuge tube. Evaporate this liquid to dryness at 30°C using a gentle nitrogen stream.

If the sample is to be analyzed immediately, dissolve the residue in 1 mL of HPLC mobile phase using a vortex mixer or ultrasonic bath. Then filter the solution through a Millex®-HV filter unit attached to a 1-mL hypodermic syringe.

If the sample cannot be analyzed immediately, it should be stored dry in a freezer.

Analysis Procedure

HPLC is used for analysis of prepared samples, and the conditions are as follows:

Chromatograph - Du Pont Model 8800
Column - Zorbax[®] ODS
Temperature - 35°C
Detector - Du Pont Model 850 (fixed-wavelength: 254 nm)
Sample Loop - 100 µL
Mobile Phase - 70% water, 30% acetonitrile
Flow - 1.5 mL/min

Under these conditions the retention time of bromacil is 8.2 minutes, and that of diuron is 23.3 minutes. The response factors for bromacil and diuron are about 1.7 and 5.6 mm/ng, respectively, normalized to 0.005 AUFS using a 1-mV, 25-cm, strip chart recorder and measuring peak heights.

Standards

Standard stock solutions are prepared by accurately weighing out 10.0 mg of bromacil and 10.0 mg of diuron into separate, 100-mL volumetric flasks. The compounds are dissolved in acetonitrile, following which the solutions are diluted to the mark with acetonitrile and mixed thoroughly.

Working standards, also used for fortifications are prepared by pipetting 1-mL aliquots of the stock solution into separate, 100-mL volumetric flasks, and evaporating the solvent

with a gentle nitrogen stream. Milli-Q® water is added to the flasks, and the flasks are swirled or put in an ultrasonic bath for a few minutes. The solutions are then diluted to the mark with Milli-Q® water and mixed thoroughly. Standard solutions of 0.50, 0.20, 0.10 and 0.050 µg/mL are prepared from the 1.0 µg/mL solutions by appropriate volumetric dilution. Mixed standards of bromacil and diuron can be prepared in the same manner.

When not in use, all standard solutions must be stored in a refrigerator. The solid bromacil and diuron standards must be kept frozen.

The stock solutions are stable for many months, and the working standards should be freshly prepared every three weeks.

Results and Discussion

The response of the UV detector at 254 nm was linear for both bromacil and diuron. Typical sets of values are shown in Tables 1 and 2. In Table 1 the response factors for bromacil have been normalized to a detector sensitivity of 0.005 AUFS, whereas in Table 2 the response factors have been normalized to a detector sensitivity of 0.01 AUFS. Normalization to the same detector sensitivity would show that the response factor for diuron is about 3.3 times greater than that for bromacil.

The results of recovery tests made on samples of natural waters, fortified with either bromacil or diuron, are shown in Tables 3 and 4.

Water samples were also fortified with both bromacil and diuron, and the results of these recovery tests are shown in Tables 5 and 6. Comparison of the data from Tables 3 and 4 with that from Tables 5 and 6 indicates that the recovery of bromacil is not affected by the simultaneous determination of bromacil and diuron. However, the recovery of diuron shows a definite trend to somewhat lower values.

Also in Tables 5 and 6 there are shown three sets of data with abnormally large standard deviations: Table 5 - diuron at 10 ppb; Table 6 - bromacil at 4 ppb; Table 6 - diuron at 4 ppb. What cannot be deduced from the data ranges shown is that in each of these three cases the data is clustered into two groups of three low values and four high values. These values are: Table 5 - diuron at 10 ppb, (53, 60, 64)(96, 98, 98, 102); Table 6 - bromacil at 4 ppb, (60, 66, 66)(84, 86, 89, 89); Table 6 - diuron at 4 ppb, (50, 54, 60)(86, 91, 95, 97). This suggests an occasional systematic error in the procedure since eliminating the low group in each case results in means and standard deviations which conform to the majority of the data (99, 2.5; 87, 2.5; 92, 4.9). The most likely source of error is the Sep-Pak® through

lack of capacity or channeling. Such a problem as this could also account for the lower diuron recoveries with the simultaneously-fortified samples.

Figures 1 and 2 are chromatograms of extracts of Stoney Run water and fortified (1 ppb) Stoney Run water, respectively. The recoveries calculated from the chromatogram of Figure 2 are 84% for bromacil and 92% for diuron.

Stability tests, of dry extracts and Sep-Paks® through which water samples had been passed, were made using individually-fortified samples of Stoney Run water. Dry extracts were obtained by processing samples completely through the procedure up to the point where mobile phase is added just prior to the HPLC analysis. Sep-Paks® were obtained by processing samples through the Sep-Pak® isolation step but excluding elution with acetonitrile and the subsequent steps. The processing and analysis of all samples were completed after the storage intervals. The results are shown in Tables 7-10. In general, the dry extracts stored well at both refrigerator (3°C) and freezer (-15°C) temperatures. The stored Sep-Paks® showed more instances of noticeable loss, and, in addition, the chromatograms of the bromacil samples were poor in the sense of showing misshapen peaks and greater interference. The conclusions to be drawn from these results are that samples can be processed completely and then held

for several days before analysis and that storage of Sep-Paks® obtained part way through the procedure is not recommended.

Similar stability tests were made using samples of Stoney Run water fortified with both bromacil and diuron. These results are shown in Tables 11 and 12. In examining this data it can be seen that storage of extracts and Sep-Paks® produces abnormally high recoveries of bromacil at the 1 ppb fortification level. As was true with the individually-fortified samples, the chromatograms showed greater noise and interference with accurate measurements of bromacil. These results show that the storage of extracts or Sep-Paks® for any appreciable period of time will probably lead to erroneously-high bromacil measurements.

In order to examine the possibility that Sep-Paks® might be conditioned in the laboratory, stored and then used directly in the field to collect bromacil and diuron from water samples, Sep-Paks® were washed with either acetonitrile or methanol (p. 7) and then stored in sealed jars in a refrigerator at 3°C for 7 days. Then they were used in the sample preparation procedures (pp. 7-8) to isolate bromacil and diuron simultaneously from fortified Stoney Run water. At this point, the Sep-Paks® were stored again in a refrigerator for either one or seven days before the compounds were eluted and analyzed (p. 8). The results are shown in Tables 13 and 14. In all cases, the measured recoveries

are good, and the losses during storage of the compounds on the Sep-Paks® are very small. In addition, the chromatograms showed clear, well-defined peaks for both compounds. These observations contrast sharply with those made in the preceding paragraphs, and it appears at this point that conditioning and storage of Sep-Paks® may play a key role in improving the procedure if Sep-Pak® storage after sample isolation is planned.

Samples of water fortified with bromacil, diuron, and both compounds together have been stored for prolonged periods of time under refrigeration (3°C), in precleaned, amber, glass bottles, and then analyzed. The results of these tests are shown in Figures 3-14. Figures 3-8 represent samples which had been fortified with either bromacil or diuron. Figures 9-14 represent samples fortified with both bromacil and diuron with Figures 9 and 12, 10 and 13, 11 and 14 being associated with the same samples. The least squares fit to the experimental points, in every case except three, shows that losses are occurring. On this basis, samples should be analyzed within a week of the collection time, if possible. This assumes proper collection and storage of the samples.

Figures 15 and 16 summarize the results obtained from storage of water samples at room temperature for two weeks. Comparison of this data with that shown in Figures 5, 8, 11, and

14 for bromacil and diuron at 10 ppb fortification shows that bromacil is lost about twice as rapidly at room temperature as at 3°C, whereas, diuron is lost at approximately the same rate.

Note: The analysis of the 56-day, simultaneously - fortified samples was performed with several changes in the HPLC system (see page 5) made necessary by the adaptation for the analysis of bromacil in soil (to be reported in another AMR).

Column - Resolve™ (Waters Part No. 85711)

Detector - Waters Model 490

Under these conditions the retention time of bromacil is 4.0 minutes and that of diuron is 9.2 minutes. The response factors for bromacil are 7.03 mm/ng at 210 nm and 5.96 mm/ng at 220 nm, normalized to 0.05 AUFS. Similarly, the response factors for diuron are 15.3 and 7.87 mm/ng, respectively. The 56-day points plotted in Figures 9-14 are the average values of the measurements at the two wavelengths.

Calculations

Quantitation is based on measurements of peak height, and the following equation is used to calculate the concentrations of bromacil and diuron in samples.

$$\text{ng/g (ppb)} = H \times \frac{1}{\text{RF}} \times V_e \times \frac{1}{V_I} \times \frac{1}{W}$$

- (a) H is the peak height in millimeters
- (b) RF is the response factor in millimeters per nanogram
- (c) V_e is the total volume of the sample extract in milliliters
- (d) V_I is the volume of sample extract injected in milliliters
- (e) W is the sample weight in grams

If the quantities described in this procedure are substituted in the equation, the result is:

$$\text{ng/g (ppb)} = \frac{0.2 H}{\text{RF}}$$

It is important to be certain that the peak height measurement is normalized to the same detector sensitivity as is used for the response factor calculation.

If samples are to be analyzed which contain bromacil or diuron at concentrations above 20 ppb, it is necessary to do one of the following:

- (1) Use a sample smaller than 50 grams.
- (2) Prepare standards of concentration greater than 1.0 µg/mL and check the response linearity.
- (3) Dilute the final extract for HPLC analysis to a volume greater than 1 mL.

In addition, it is necessary to demonstrate recovery at the higher level by analysis of fortified samples.

Conclusion

Bromacil and diuron can be effectively measured in water at levels as low as 1 ppb by means of a simple isolation and analysis procedure. No interferences were found in the types of water tested.

Use of an auto-sampler for the HPLC analysis leaves the sample processing procedure as the step which determines throughput. Under favorable conditions it should be possible to process 16 samples per day, including the analysis.

Table 1

Detector Response for Bromacil

<u>Concentration</u> <u>(μg/mL)</u>	<u>Peak Height</u> <u>(mm/AUFS)</u>	<u>Response Factor</u> <u>(mm/ng)</u>
0.05	9/0.005	1.80
0.10	17/0.005	1.70
0.20	17/0.01	1.70
0.50	44/0.01	1.76
1.0	44/0.02	1.76
Mean		1.74
Standard Deviation		0.04

Table 2

Detector Response for Diuron

<u>Concentration</u> <u>($\mu\text{g/mL}$)</u>	<u>Peak Height</u> <u>(mm/AUFS)</u>	<u>Response Factor</u> <u>(mm/ng)</u>
0.05	29/0.005	2.90
0.10	58/0.005	2.90
0.20	57/0.01	2.85
0.50	144/0.01	2.88
1.0	147/0.02	2.94
	Mean	2.89
	Standard Deviation	0.03

Table 3

Bromacil Recovery*

<u>Source</u>	<u>Fortification (ppb)</u>	<u>Recovery (%)</u>		
		<u>Mean</u>	<u>SD</u>	<u>Range</u>
Stoney Run	1.0	97	8.6	90 - 106
New Castle County	2.0	88	4.7	85 - 97
Delaware	4.0	85	4.9	78 - 92
	10	85	3.4	80 - 89
	20	88	4.8	82 - 96
Lums Pond	1.0	92	6.3	88 - 101
New Castle County	2.0	86	4.4	81 - 94
Delaware	4.0	85	5.7	77 - 92
	10	85	4.4	78 - 92
	20	86	5.3	80 - 93

*N = 7 for each water at each fortification level.

Table 4

Diuron Recovery*

<u>Source</u>	<u>Fortification (ppb)</u>	<u>Recovery (%)</u>		
		<u>Mean</u>	<u>SD</u>	<u>Range</u>
Stoney Run	1.0	96	4.1	90 - 104
New Castle County	2.0	102	4.4	96 - 107
Delaware	4.0	101	6.4	89 - 107
	10	97	5.0	90 - 104
	20	94	5.0	87 - 101
Lums Pond	1.0	97	5.7	90 - 104
New Castle County	2.0	98	5.3	90 - 104
Delaware	4.0	97	5.6	86 - 101
	10	96	6.1	85 - 104
	20	93	6.4	84 - 103

*N = 7 for each water at each fortification level except
N = 6 for Stoney Run - 2.0 ppb fortification.

Table 5

Bromacil and Diuron Recoveries from Stoney Run Water*

<u>Compound</u>	<u>Fortification (ppb)</u>	<u>Recovery (%)</u>		
		<u>Mean</u>	<u>SD</u>	<u>Range</u>
Bromacil	1.0	81	0	0
Diuron	1.0	91	5.7	81 - 96
Bromacil	1.0	84	6.6	72 - 95
Diuron	10	92	5.6	84 - 98
Bromacil	10	82	5.9	72 - 90
Diuron	1.0	91	6.8	81 - 102
Bromacil	4.0	91	7.0	78 - 100
Diuron	4.0	89	7.6	74 - 95
Bromacil	10	86	8.8	74 - 95
Diuron	10	82	21	53 - 102

*N=7 for each fortification level.

Table 6

Bromacil and Diuron Recoveries from Lums Pond Water*

<u>Compound</u>	<u>Fortification (ppb)</u>	<u>Recovery (%)</u>		
		<u>Mean</u>	<u>SD</u>	<u>Range</u>
Bromacil	1.0	81	5.9	72 - 84
Diuron	1.0	88	5.0	78 - 92
Bromacil	1.0	82	6.9	70 - 94
Diuron	10	93	5.0	85 - 100
Bromacil	10	84	3.7	78 - 89
Diuron	1.0	89	5.7	82 - 96
Bromacil	4.0	77	12	60 - 89
Diuron	4.0	76	21	50 - 97
Bromacil	10	84	4.8	79 - 90
Diuron	10	93	5.7	84 - 99

*N=7 for each fortification level.

Table 7

Bromacil Refrigerator (3°C) Storage

<u>Sample</u>	<u>Bromacil Recovery (%)</u>		
	<u>1 ppb</u>	<u>2 ppb</u>	<u>10 ppb</u>
Extract			
0 day	94	82	87
1 day	106	82	88
3 day	106	88	101
7 day	92	92	85
Sep-Pak®			
0 day	84	82	89
1 day	94	82	91
3 day	94	76	84
7 day	68	98	98

Table 8

Bromacil Freezer (-15°C) Storage

<u>Sample</u>	<u>Bromacil Recovery (%)</u>		
	<u>1 ppb</u>	<u>2 ppb</u>	<u>10 ppb</u>
Extract			
0 day	104	91	100
1 day	104	110	90
3 day	106	83	85
7 day	89	89	92
Sep-Pak®			
0 day	94	94	83
1 day	106	94	85
3 day	82	94	104
7 day	80	86	94

Table 9

Diuron Refrigerator (3°C) Storage

<u>Sample</u>	<u>Diuron Recovery (%)</u>		
	<u>1 ppb</u>	<u>2 ppb</u>	<u>10 ppb</u>
Extract			
0 day	96	102	97
1 day	92	89	96
3 day	96	92	84
7 day	90	93	89
Sep-Pak®			
0 day	96	102	97
1 day	94	94	99
3 day	96	79	97
7 day	98	91	96

Table 10
Diuron Freezer (-15°C) Storage

<u>Sample</u>	<u>Diuron Recovery (%)</u>		
	<u>1 ppb</u>	<u>2 ppb</u>	<u>10 ppb</u>
Extract			
0 day	96	102	97
1 day	100	85	93
3 day	96	89	99
7 day	97	93	89
Sep-Pak®			
0 day	96	102	97
1 day	94	86	96
3 day	96	82	93
7 day	90	84	88

Table 11
Bromacil and Diuron Refrigerator (3°C) Storage

<u>Sample</u>	<u>Bromacil/Diuron Recovery (%)</u>		
	<u>1 ppb</u>	<u>2 ppb</u>	<u>10 ppb</u>
Extract			
0 day	94/96	82/102	87/97
1 day	142/106	95/94	95/101
3 day	145/103	103/93	85/95
7 day	112/106	99/94	96/105
Sep-Pak®			
0 day	84/96	82/102	89/97
1 day	106/102	83/91	90/103
3 day	92/102	81/91	88/104
7 day	96/92	85/86	85/100

Table 12
Bromacil and Diuron Freezer (-15°C) Storage

<u>Sample</u>	<u>Bromacil/Diuron Recovery (%)</u>		
	<u>1 ppb</u>	<u>2 ppb</u>	<u>10 ppb</u>
Extract			
0 day	104/96	91/102	100/97
1 day	106/103	89/90	88/96
3 day	121/100	103/99	87/96
7 day	123/94	93/86	84/89
Sep-Pak®			
0 day	94/96	94/102	83/97
1 day	94/102	77/88	83/95
3 day	92/98	76/88	84/94
7 day	85/96	79/86	85/97

Table 13
Acetonitrile Pretreatment

<u>Compound (Fortification)</u>	<u>Recovery (%)*</u>	
	<u>Day 1</u>	<u>Day 7</u>
Bromacil (1 ppb)	98, 86 (92)	88, 88 (88)
Diuron (1 ppb)	98, 101 (100)	88, 92 (90)
Bromacil (10 ppb)	85, 85 (85)	80, 83 (82)
Diuron (10 ppb)	91, 91 (91)	89, 90 (90)

*Parenthetical values are means.

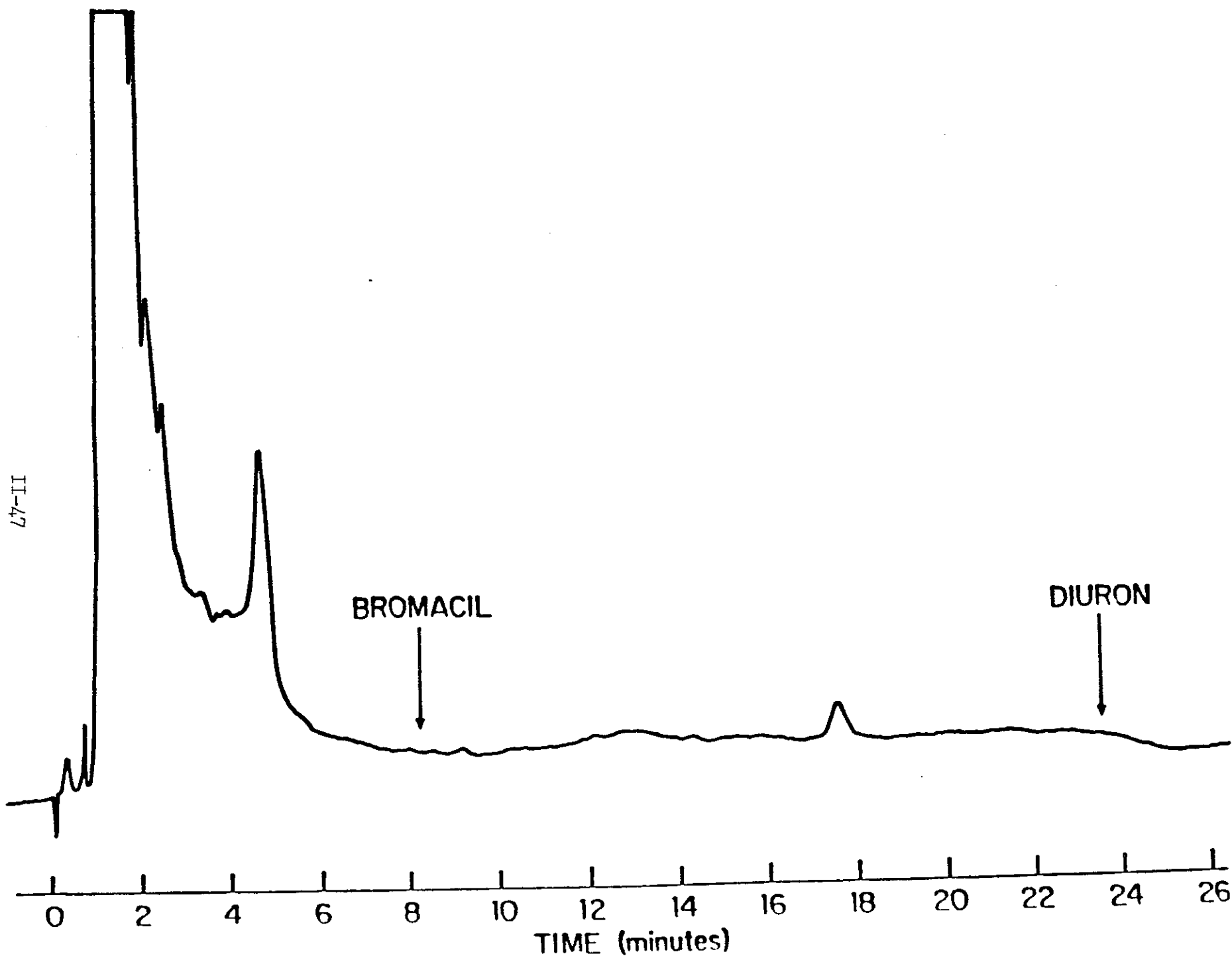
Table 14
Methanol Pretreatment

<u>Compound (Fortification)</u>	<u>Recovery (%)*</u>	
	<u>Day 1</u>	<u>Day 7</u>
Bromacil (1 ppb)	98, 98 (98)	88, 100 (94)
Diuron (1 ppb)	91, 94 (93)	92, 92 (92)
Bromacil (10 ppb)	83, 85 (84)	83, 86 (85)
Diuron (10 ppb)	88, 91 (90)	92, 92 (92)

*Parenthetical values are means.

FIGURE 1

CHROMATOGRAM OF EXTRACT OF STONEY RUN WATER
(0.005 AUFS)



II-47

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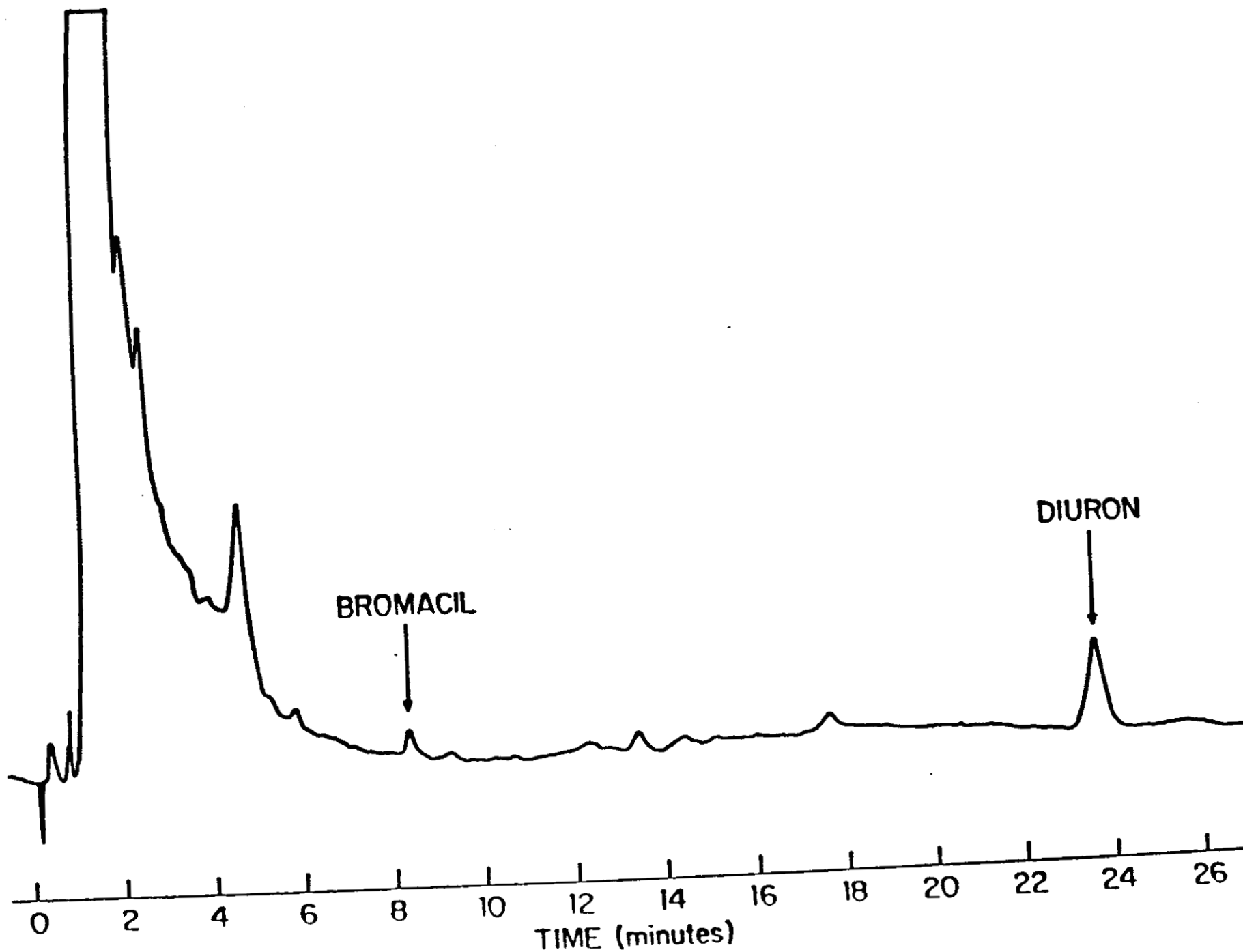
FIGURE 2

CHROMATOGRAM OF EXTRACT OF FORTIFIED STONEY RUN

WATER - 1 ppb BROMACIL AND 1 ppb DIURON

(0.005 AUFS)

67-II

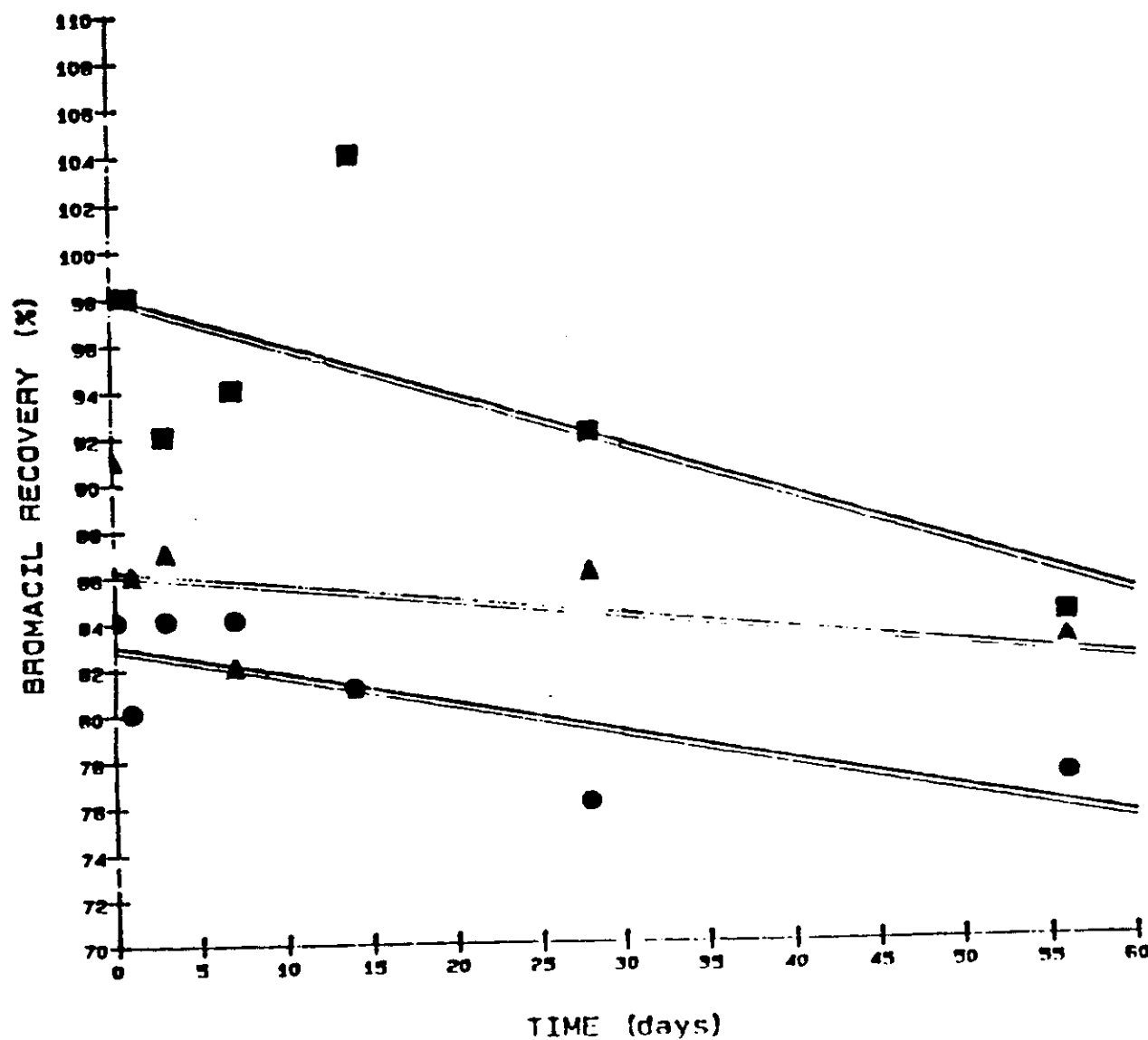


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FIGURE 3

STABILITY OF BROMACIL IN REFRIGERATED WATER
(MILLI-Q®)

MILLIPORE WATER



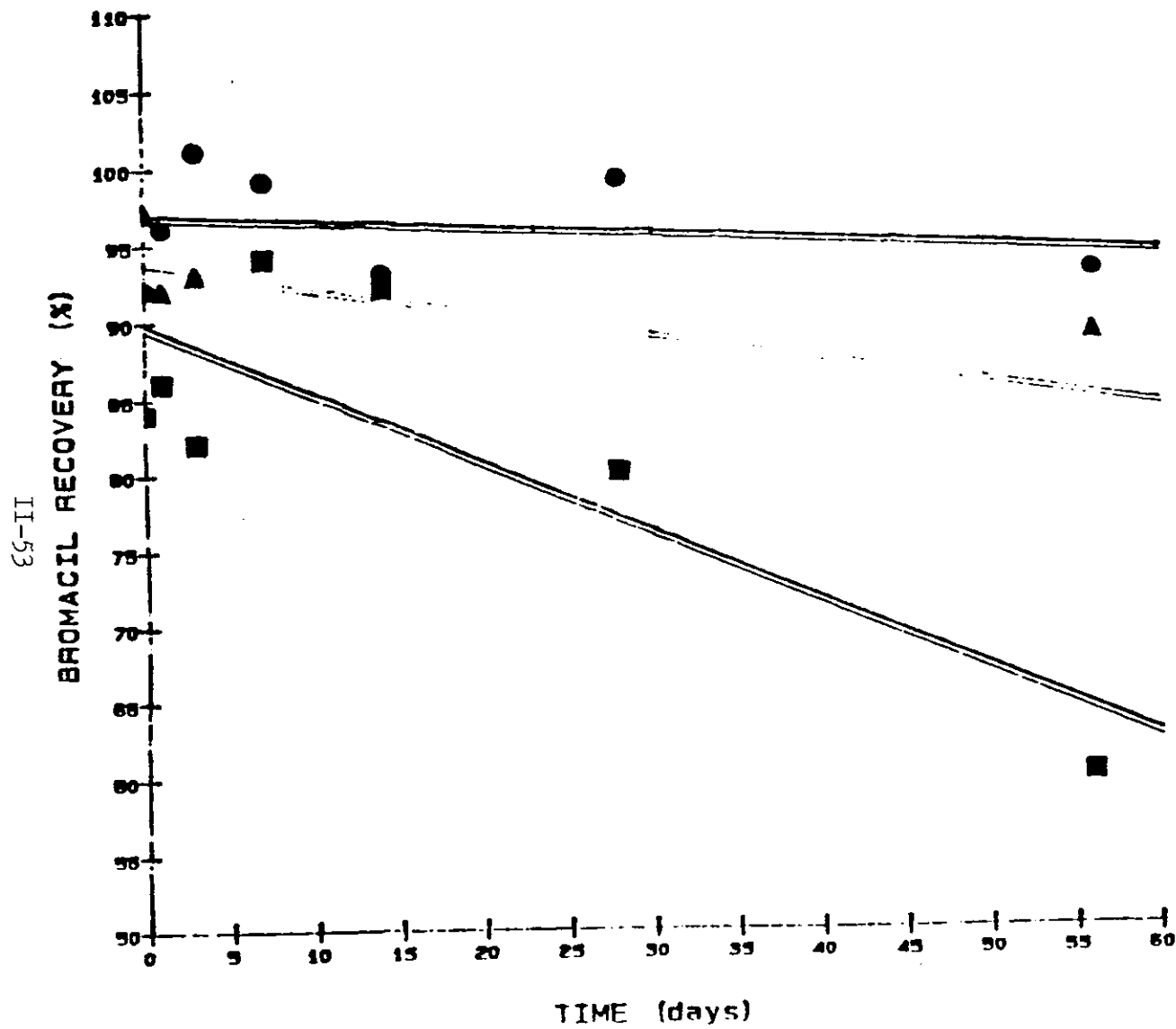
■ 1 ppb
 ▲ 2 ppb
 ● 10 ppb
 $-0.218058 \times X + 97.966905$
 $-0.068439 \times X + 86.208545$
 $-0.128921 \times X + 82.864622$

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FIGURE 4

STABILITY OF BROMACIL IN REFRIGERATED WATER
(FILTERED STONEY RUN)

FILTERED STONEY RUN WATER



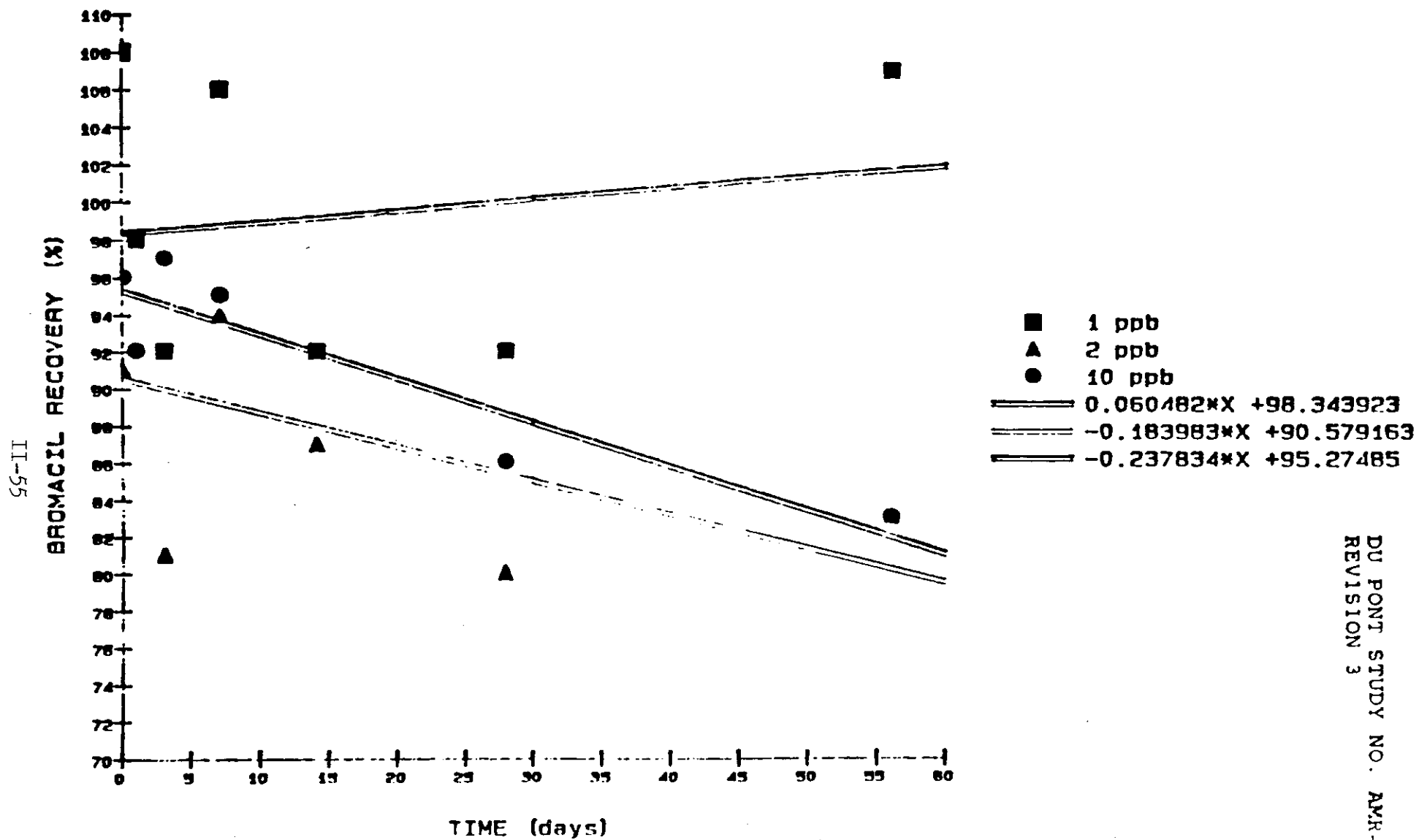
- 1 ppb
- ▲ 2 ppb
- 10 ppb
- $-0.452952 \times X + 89.624539$
- $-0.153194 \times X + 93.52831$
- $-0.042608 \times X + 96.806331$

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REVISION 3

FIGURE 5

STABILITY OF BROMACIL IN REFRIGERATED WATER
(STONEY RUN)

STONEY RUN WATER

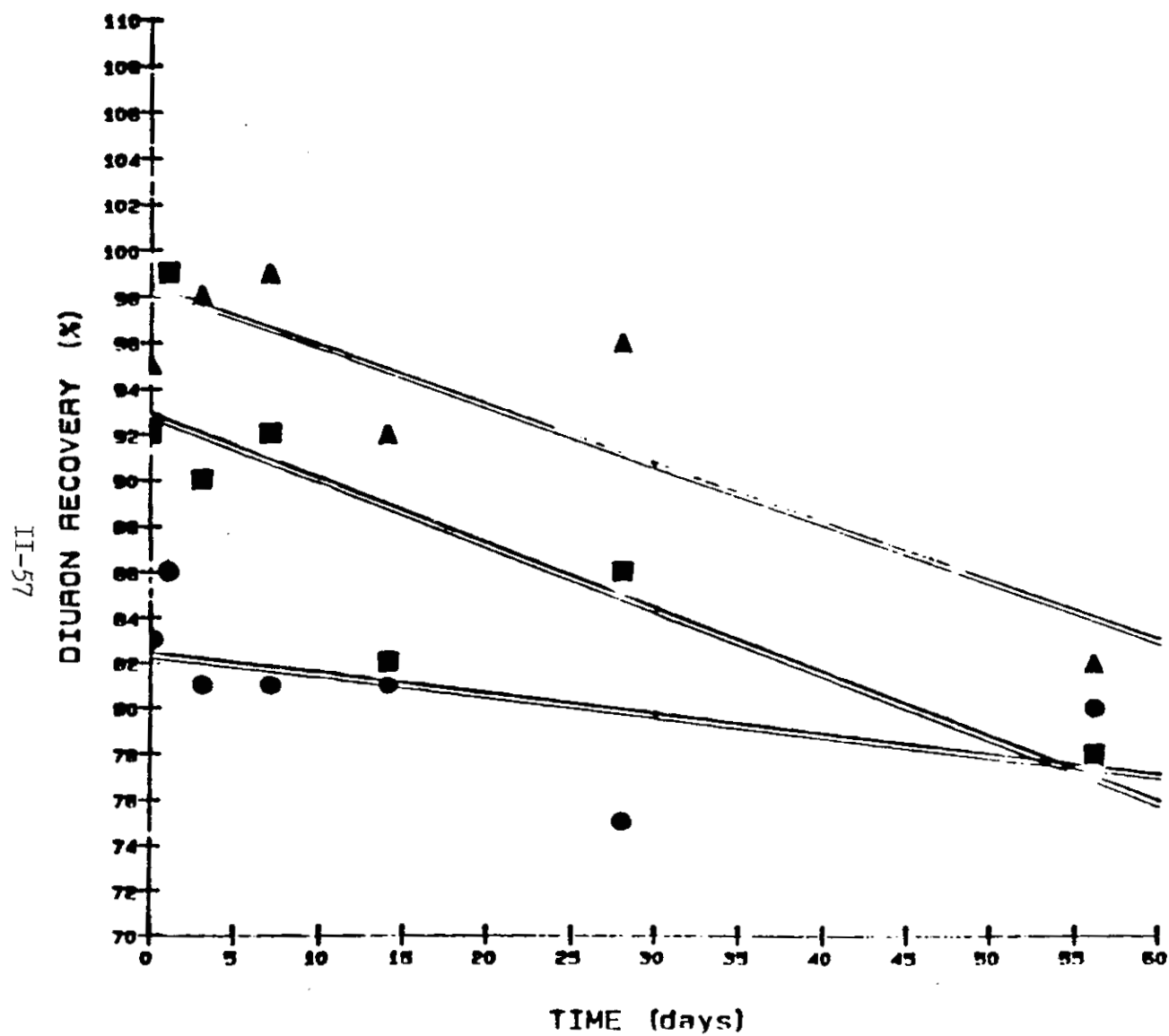


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REVISION 3

FIGURE 6

STABILITY OF DIURON IN REFRIGERATED WATER
(MILLI-Q®)

MILLIPORE WATER



- 1 ppb
- ▲ 2 ppb
- 10 ppb
- $-0.28321 \times X + 92.838561$
- $-0.257784 \times X + 98.442631$
- $-0.088388 \times X + 82.376326$

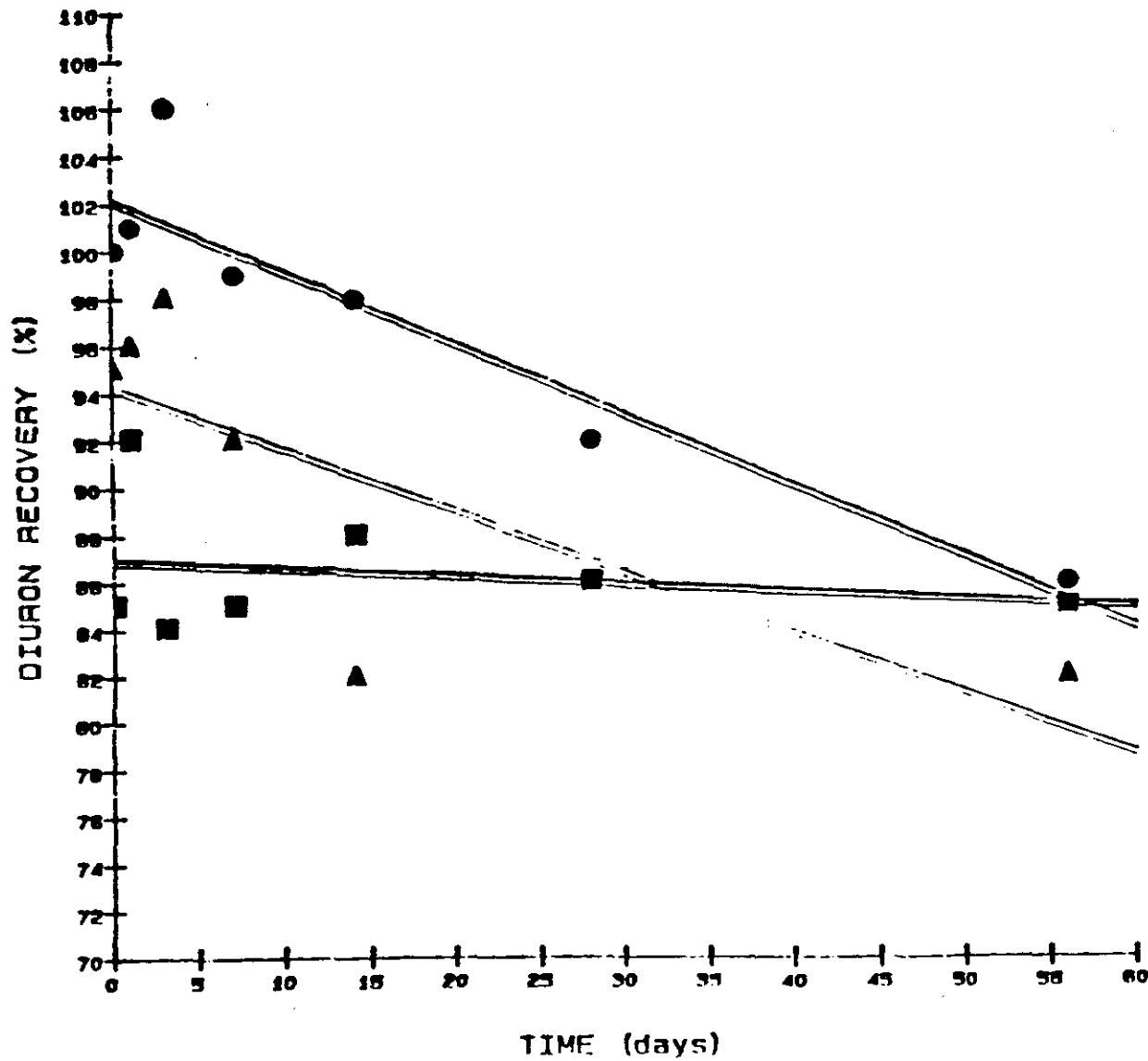
DU PONT STUDY NO. AMN-553-B6
REVISION 3

FIGURE 7

STABILITY OF DIURON IN REFRIGERATED WATER
(FILTERED STONEY RUN)

FILTERED STONEY RUN WATER

65-II



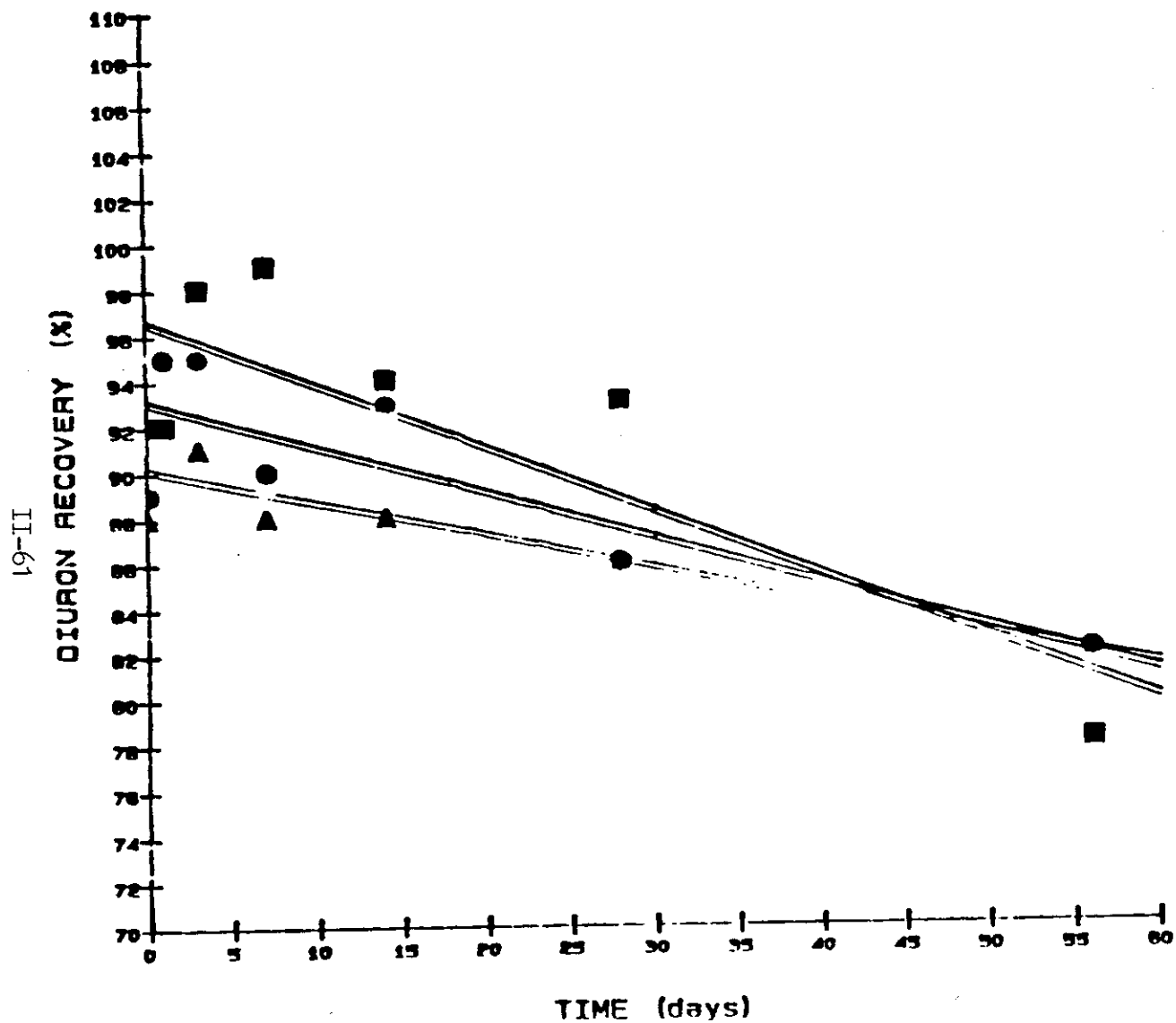
- 1 ppb
- ▲ 2 ppb
- 10 ppb
- $-0.03298 \times X + 86.942113$
- $-0.259744 \times X + 94.187442$
- $-0.300161 \times X + 102.102514$

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FIGURE 8

STABILITY OF DIURON IN REFRIGERATED WATER
(STONEY RUN)

STONEY RUN WATER



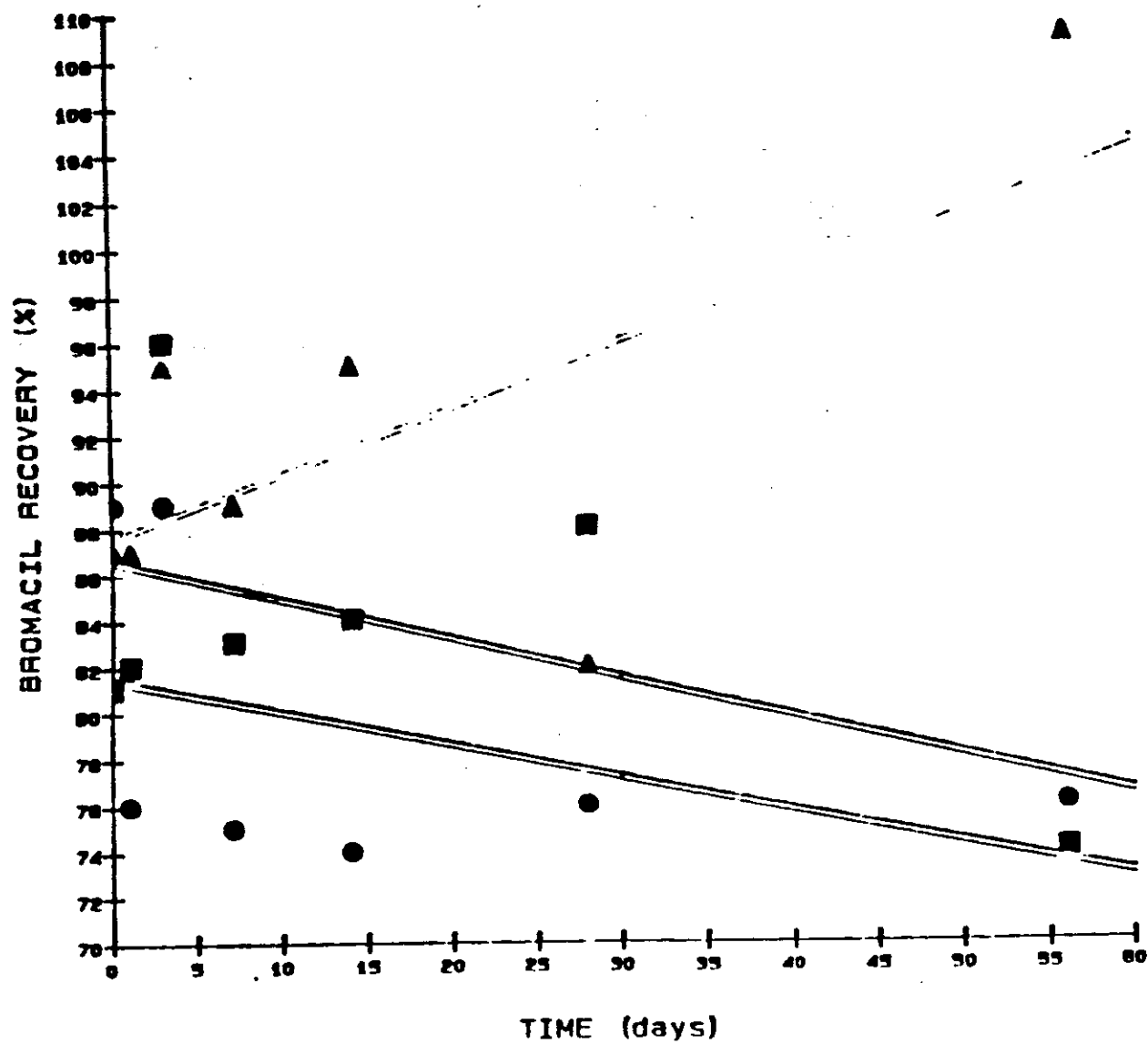
- 1 ppb
- ▲ 2 ppb
- 10 ppb
- $-0.279347 \times X + 96.635551$
- $-0.146679 \times X + 90.141144$
- $-0.200992 \times X + 93.129728$

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FIGURE 9

STABILITY OF BROMACIL IN REFRIGERATED WATER
(MILLI-Q®)

MILLIPORE WATER



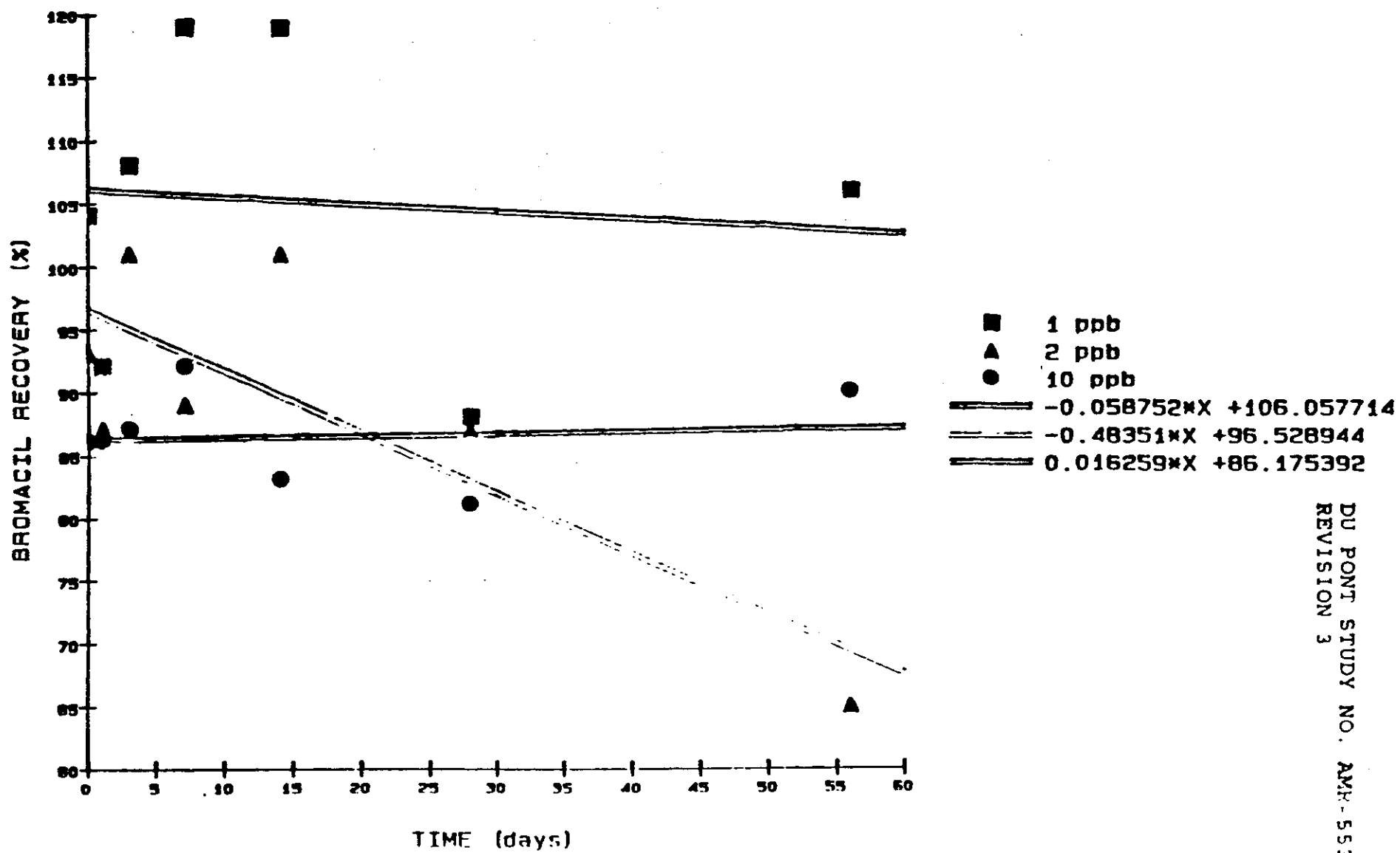
- 1 ppb
- ▲ 2 ppb
- 10 ppb
- $-0.169915 \times X + 86.645814$
- $0.281308 \times X + 87.619638$
- $-0.142931 \times X + 81.511358$

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FIGURE 10

STABILITY OF BROMACIL IN REFRIGERATED WATER
(FILTERED STONEY RUN)

FILTERED STONEY RUN WATER



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FIGURE 11

STABILITY OF BROMACIL IN REFRIGERATED WATER
(STONEY RUN)

STONEY RUN WATER

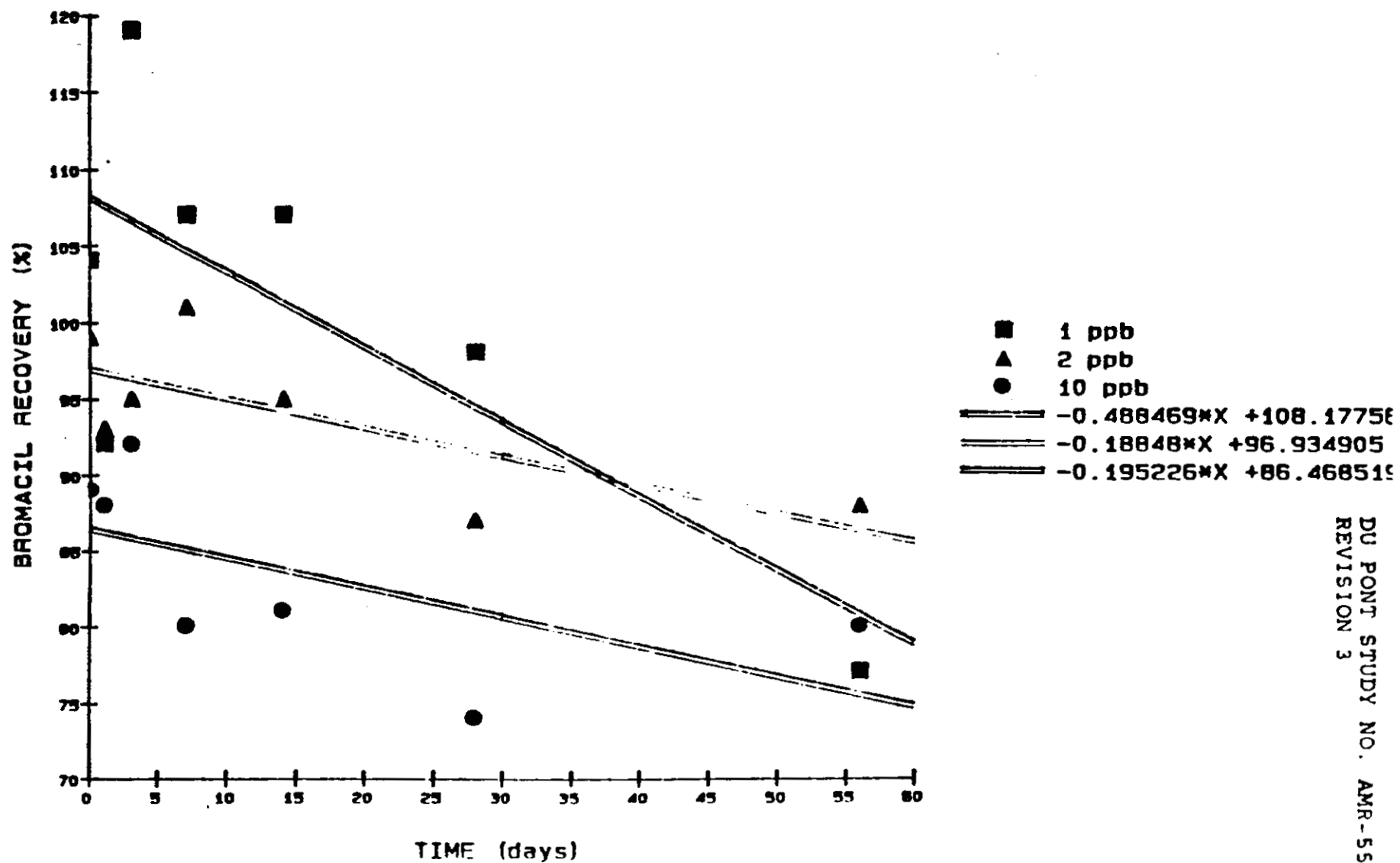
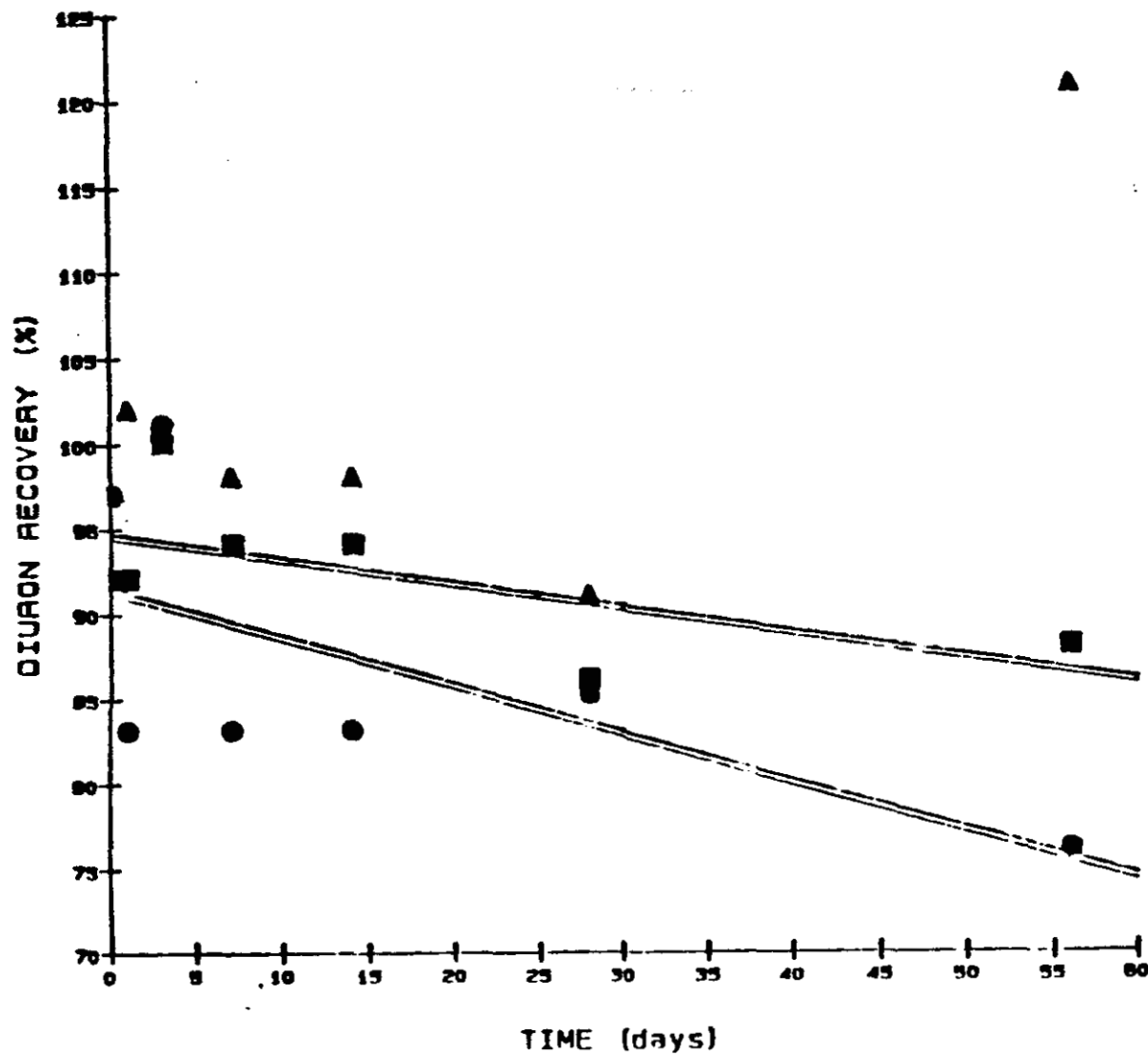


FIGURE 12

STABILITY OF DIURON IN REFRIGERATED WATER
(MILLI-Q®)

MILLIPORE WATER



■ 1 ppb
 ▲ 2 ppb
 ● 10 ppb
 $-0.144142 \times X + 94.530212$
 $0.307714 \times X + 96.351303$
 $-0.283499 \times X + 91.271621$

DU PONT STUDY NO. AMR-5;
 REVISION 3

FIGURE 13

STABILITY OF DIURON IN REFRIGERATED WATER
(FILTERED STONEY RUN)

FILTERED STONEY WATER

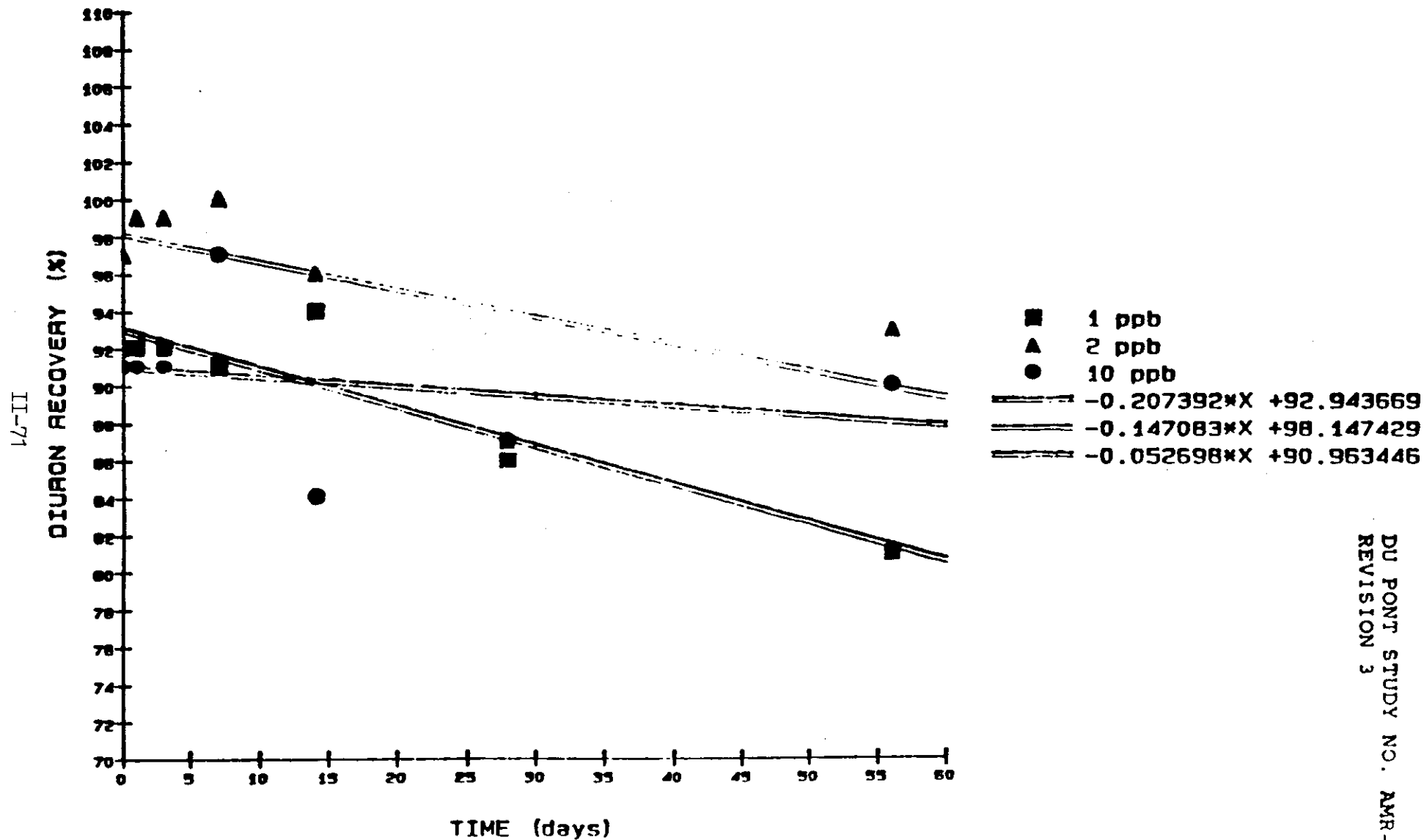
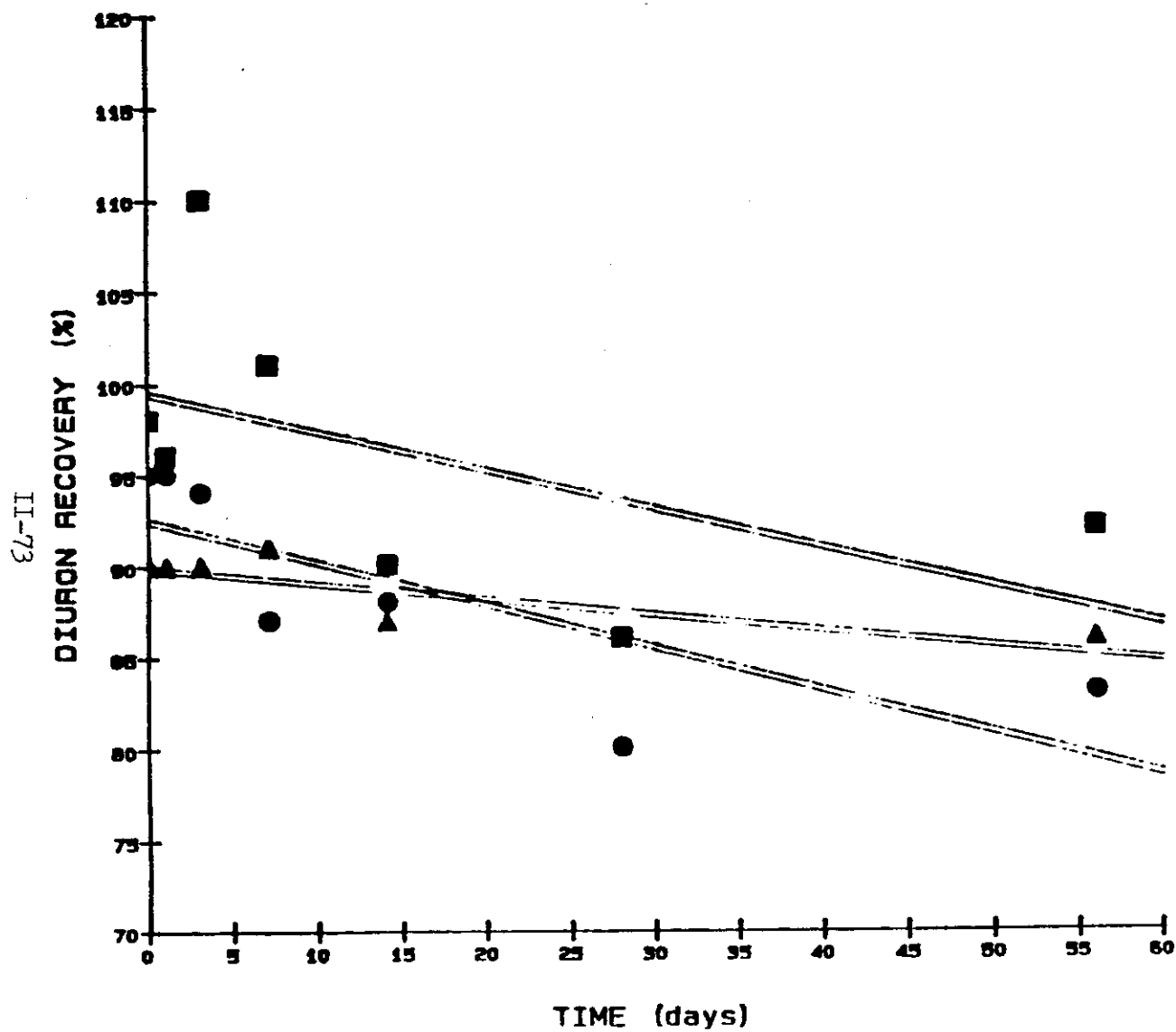


FIGURE 14

STABILITY OF DIURON IN REFRIGERATED WATER
(STONEY RUN)

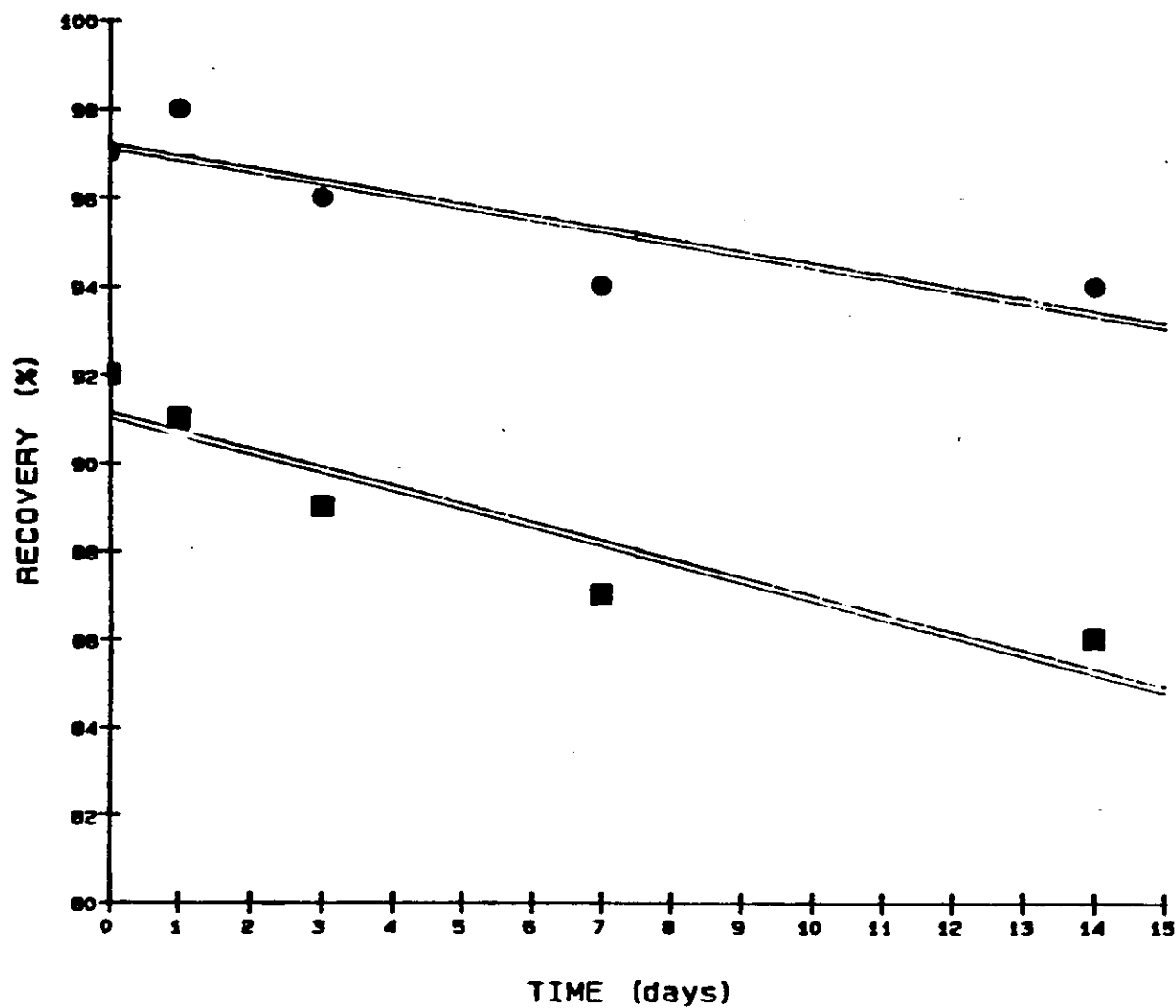
STONEY RUN WATER



- 1 ppb
- ▲ 2 ppb
- 10 ppb
- $-0.212523 \times X + 99.452145$
- $-0.086889 \times X + 89.924412$
- $-0.233856 \times X + 92.498616$

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ROOM TEMPERATURE STORAGE



■ BROMACIL
 ● DIURON
 $-0.415385 \times X + 91.076923$
 $-0.269231 \times X + 97.146154$

STONEY RUN WATER WITH 10 ppb FORTIFICATION

DU PONT STUDY NO. AMR-553-86
REVISION 3

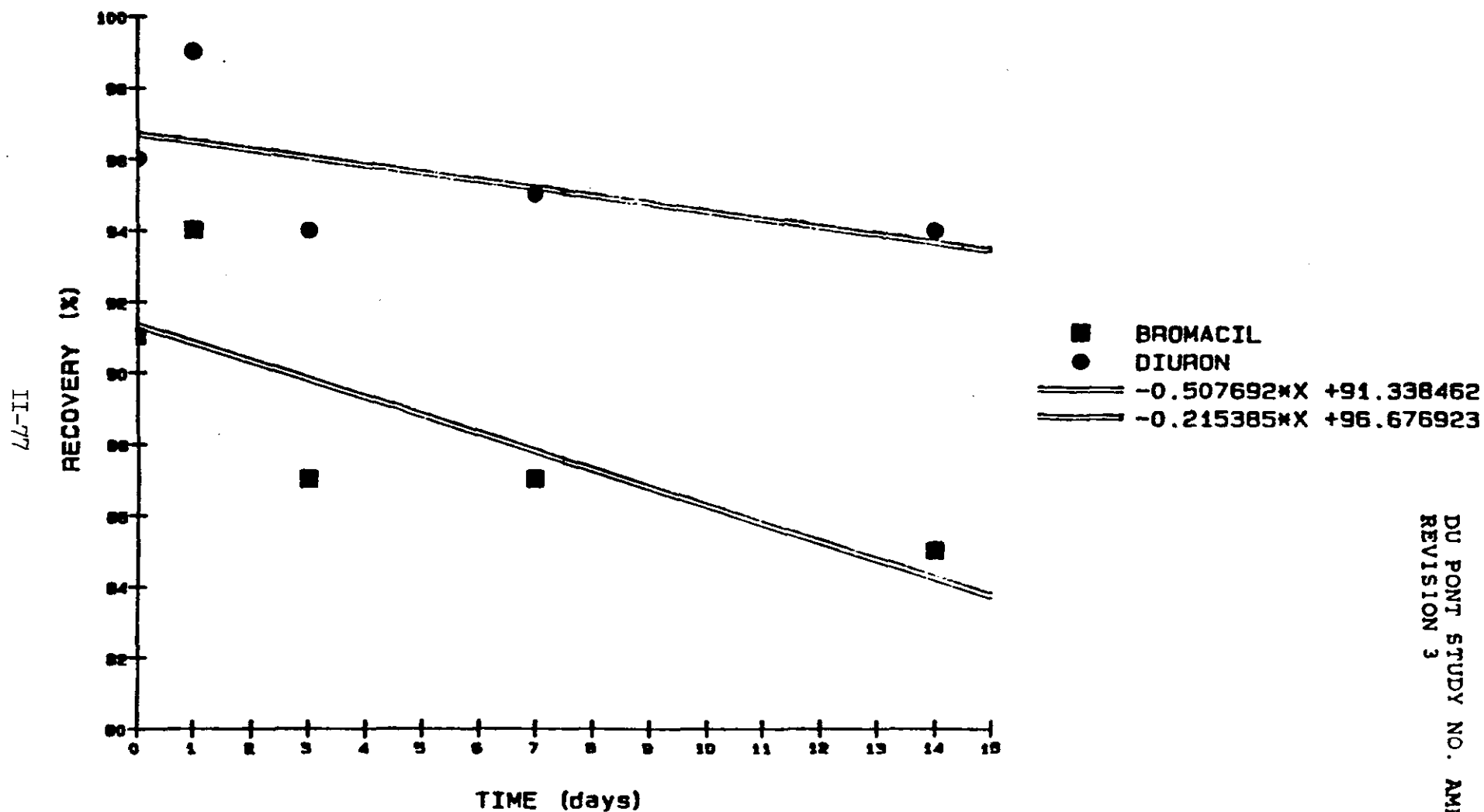
FIGURE 15

STABILITY OF BROMACIL AND DIURON IN
ROOM TEMPERATURE WATER

FIGURE 16

STABILITY OF BROMACIL AND DIURON IN
ROOM TEMPERATURE WATER

ROOM TEMPERATURE STORAGE



LUMS POND WATER WITH 10 ppb FORTIFICATION

DU PONT STUDY NO. AMR-553-86
REVISION 3

FIELD USE OF SEP-PAK CARTRIDGES

The processing procedure described on pp. 8-9 for the isolation of bromacil from water has been extended to field use, thereby eliminating the need for collection and shipping of water samples. The details of the evaluation can be found in the report of May 6, 1988 (to R. A. Jackson from E. W. Zahnow).

Edward W. Zahnow August 12, 1988
Edward W. Zahnow, Date

Materials

Sep-Pak C₁₈ cartridges (Part No. 51910; available from Waters Associates, Milford, Massachusetts).

Methanol (HPLC grade).

Water (Milli-Q or equivalent).

Hypodermic syringes, 5 mL and 50 mL, glass or plastic.

Plastic zip-lock bags.

Glass jars with lids.

Plastic refrigerator dishes.

Pretreatment Procedure

In order for a Sep-Pak to function properly it is essential that it be preconditioned with an organic solvent followed by a water rinse.

For field use it is recommended that 5 mL of methanol be put through the cartridge first followed by 5 mL of high-purity water. It is convenient to use a 5-mL syringe for this procedure, drawing the methanol into the syringe, adjusting the volume, and then attaching to the longer end (inlet) of the cartridge. The methanol should go through the cartridge at a steady rate of 5-10 mL/minute, such that discrete drops can be seen forming at the outlet.

At the completion of this step the Sep-Pak is disconnected from the syringe before the plunger of the syringe is withdrawn. Then the syringe is rinsed with water several times, and finally it is filled with 5 mL of water which are put through the cartridge as described previously for methanol.

When all of the water has been passed through, the syringe is disconnected once again, the plunger is withdrawn to the 1-mL

mark, the syringe is reconnected to the cartridge, and 1 mL of air is put through the cartridge to expel the small volume of water remaining.

A vacuum manifold can also be used, if available, for the pretreatment steps. When a number of cartridges are treated simultaneously, it is important to note and regulate the relative liquid flow rates. Also, large volumes of air should not be drawn through the cartridges at any time.

After the pretreatment is complete, the cartridges are stored together in a glass jar of appropriate size fitted with a lid which seals tightly.

Shipping and Storage

No special precautions are required, and storage at ambient temperatures is satisfactory (not below freezing). However, it is not advisable to allow the jar filled with Sep-Paks to sit in direct sunlight for extended periods of time.

Field Use

To load a sample in the field, the plunger is withdrawn from the barrel of a 50-mL syringe, and the barrel is filled directly from the well outlet. The plunger is immediately inserted into the barrel, and the volume is adjusted to 50 mL.

A preconditioned Sep-Pak is attached to the syringe by the longer end, and the water is put through at a steady rate so that discrete drops form at the outlet of the Sep-Pak.

When all of the water has been passed through, the Sep-Pak is disconnected from the syringe and placed into a small zip-lock bag marked with the appropriate sample number. This bag is placed in a plastic refrigerator dish along with other samples that have been collected, and the dish is stored on crushed ice in a small cooler.

Shipment

It is preferable that the samples be kept on crushed ice during shipping and that they be stored in a refrigerator when they arrive in the laboratory.

Freezing is not recommended.

Analysis

The samples are processed as described on page 9, beginning at line 7.

DU PONT STUDY NO. AMR-553-86
REVISION 3
AUGUST 10, 1988

STORAGE LOCATION OF RAW DATA, REPORTS

E. I. du Pont de Nemours and Company, Inc.
Agricultural Products Department
Experimental Station
Residue Studies Groups' Archives
Wilmington, Delaware 19898

A P P E N D I X I I I

SUMMARY OF CIBA-GEIGY'S PESTICIDE ANALYTICAL METHOD

RESIDUE CHEMISTRY DEPARTMENT
AGRICULTURAL DIVISION
CIBA-GEIGY CORPORATION
GREENSBORO, NORTH CAROLINA

RESIDUE TEST REPORT

PAGE 2 OF 2

TEST NUMBER: RS-WM-005-90

REPORT NO.: 001

Analytical Method

EXTRACTION: Prepare standard water samples by spiking tap water with various concentrations of simazine. Place bond elute cartridges containing 500 mg C-18 bonded silica on 10-position vacuum manifold. Activate cartridges by successive treatment with 5 ml methanol, methanol in water (1:1) and water. Aspirate 500 ml water through at 3-4 ml/min. and air dry 5 min. Samples were decanted from bottles but not filtered. Elute cartridges into collection vials with 5 ml methylene chloride. Concentrate to 0.5 ml under stream of nitrogen.

GC/MSD Parameters

Components	Description and Operation Conditions	
GC	Hewlett-Packard 5890	
Capillary Column	DB-5	30m x .25mm
Injection Mode	Splitless	.5 min. purge
Carrier Gas	Helium	10 PSI
Temperature	Transfer Line	275°C
	Injection Port	250°C
	Oven Initial	125°C
	Rate	5°/min. to 160°; 10°/min. to 200° Hold 2 min.; 40°/min. to 275°C
	Final Temperature	275°C
	Final Time	1 min.
Mass Spectrometer	Hewlett-Packard 5970	
Ion Source	Electron Impact	70 eV
	Source Temperature	275°C
Selective Ion Monitoring	Simazine	173,186,201
Solvent Delay		6 min.

PROCEDURAL RECOVERIES

- I. Control (tap) + 10 ppb simazine = 107%
" " + 100 ppb simazine = 81%
" " = 200 ppb simazine = 81%

Source: Ciba-Geigy's Residue Test Report dated 3/27/90

- II. Control + 1.0 ppb simazine = 143%
" + 25.0 ppb simazine = 122%

Source: Ciba-Geigy's Residue Test Report dated 5/31/90

A P P E N D I X I V

SUMMARY OF APPL'S PESTICIDE ANALYTICAL METHOD

APPL, INC.

AGRICULTURE & PRIORITY POLLUTANTS LABORATORIES, INC.

4203 WEST SWIFT AVENUE • FRESNO, CALIFORNIA 93722 • PHONE (209) 275-2175

Calif. Dept. of Food and Ag.
Environmental Monitoring and
Pest Management
1220 "N" St., Room A-149
Sacramento, CA 95814
Attn: Adolf Braun

March 23, 1990

Re: Aqueous samples submitted on 01/23/90 for Simazine,
Bromacil, and Diuron.

The water samples indicated above were analyzed as outlined below:

- A) Samples were received and logged into the laboratory on 01/23/90. They were placed in refrigerated storage prior to extraction later that day.
- B) Each sample was decanted into a graduated cylinder for volume measurement, then placed into a separatory funnel for analysis.
- C) Simazine and Bromacil were analyzed by method EPA-507, (methylene chloride liquid-liquid extraction and GC-NPD detection and quantitation. Dual column confirmation was used).
- D) Diuron was analyzed by method EPA-632, (methylene chloride liquid-liquid extraction, methanol solvent replacement, and using LC/MS as detection-semi quantitation and LC-U.V. as primary quantitation).

If there are any questions regarding the analytical procedures used for these determination, please contact APPL Labs (209/275-2175).

Sincerely
APPL Laboratories, Inc.



Glen Brown
Marketing/Customer Service

GB/sg